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1. Introduction

The selective oxidation of abundant and cheap hydrocarbons into the corresponding higher-valued compounds, such as alcohols and aldehydes, is of great importance in organic synthesis.^{1,2} Although various catalysts and oxidants have been developed, the activation of the C–H bond in hydrocarbons still remains one of the most challenging reactions.³ The liquid phase oxidative conversion of ethylbenzene (EB) is attracting substantial attention to produce acetophenone (AcPO) which is an important intermediate for chemical industries.⁴ The conventional reactions exhibit advanced reaction efficiency by

Atomically dispersed cobalt on graphitic carbon nitride as a robust catalyst for selective oxidation of ethylbenzene by peroxymonosulfate[†]

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The development of a highly efficient strategy for the activation of the C–H bond in hydrocarbons is one of the most challenging tasks facing the chemical industries. The synthesis of novel catalysts with atomically dispersed active centers is highly desirable to achieve the maximized atom efficiency. Here we report the controllable preparation of a Co-based single-atom catalyst anchored on a graphitic carbon nitride support (SACo@g-C₃N₄) with 3.17 wt% Co content, which is successfully applied for the selective oxidation of ethylbenzene (EB) to derive acetophenone (AcPO) *via* the activated peroxymonosulfate (PMS) oxidant. The Co atoms are chemically bonded with the N atoms of g-C₃N₄ and present exceptional stability and reusability to resist the applied acidic-oxidative environment. Both the EB conversion and AcPO selectivity were over 95% in this highly selective SACo@g-C₃N₄/PMS system under mild reaction conditions. The selective conversion of EB into AcPO is attributed to the oxidative radicals generated from the decomposition of PMS molecules *via* the electron transfer between Co atoms and PMS. Sulfate radicals (SO₄⁻⁻) make a greater contribution than others to activate the C–H bond in EB oxidation. This work uncovers a facile and scalable approach for the synthesis of a robust Co-based single atom catalyst (SAC) on a g-C₃N₄ support and unveils its potential in the oxidation of hydrocarbons *via* a highly efficient and environmentally benign PMS activation.

adopting stoichiometric oxidants such as permanganate and dichromate.⁵ However, these processes produce a large amount of hazardous waste. As an alternative, heterogeneous catalysis with immobilized transition-metal active sites and environmentally benign oxidants has been extensively investigated. The catalytic efficiency of the reported metal-based catalysts heavily depends on the dispersion level and the stability of the metallic active sites. Nevertheless, transition-metal based catalysts usually suffer from severe metal leaching during the liquid phase reactions, especially in an acidic oxidative environment, which impedes their application as robust catalysts.

Recently, the development of single-atom catalysts (SACs) has been one of the most active research fields, as they exhibit superior efficiency and excellent selectivity in energy-related or environmental catalysis, far exceeding those of metal nanoparticle catalysts.⁶⁻⁸ In addition, the atomic metal active sites are chemically bonded with the supporting materials, thus significantly enhancing the stability under harsh reaction conditions compared with nanoclusters or nanoparticles.⁹ Tremendous efforts have been made to anchor noble-metal or transition-metal single atoms on carbon-based materials such as graphene, carbon nanotubes and carbon nitride, since carbocatalysts not only exhibit high resistance to an acidic/basic environment but also have unique chemical and electrochemical properties to enhance the electron transfer behavior

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to accomplish the catalytic reactions.^{10,11} Specifically, $g-C_3N_4$ is a layered material, similar to graphene, and has a medium band gap and serves as an effective catalyst for a broad variety of reactions.^{12,13} It also possesses advantages including good chemical stability and low cost. Furthermore, the rich N environment can provide sufficient N atoms to coordinate with metal, enabling $g-C_3N_4$ as an excellent supporting material for metallic single atoms. Nevertheless, there are still many challenges remaining to be overcome, for instance, how to achieve a feasible, controllable and low-cost approach for single atom synthesis. The realization of such an approach is highly attractive and will provide new possibilities of potential applications for efficient catalysis.¹⁴

Many oxidizing agents including oxygen, ozone, and liquid phase peroxides (i.e. hydrogen peroxide, tert-butyl hydroperoxide (TBHP) and halides) are employed as terminal oxidants to stimulate the C-H activation in a variety of hydrocarbon oxidative reactions.¹⁵⁻²⁰ In the case of oxygen, the resultant hydrocarbon conversion is low due to the difficulty in activating O₂ due to its triplet ground state structure, which usually requires high temperature/pressure or the presence of cocatalysts to assist the activation of the inert C-H bonds.4,21,22 On the other hand, the liquid oxidants and ozone cause a big concern for transportation and storage. Therefore, the application of inexpensive and stable solid-phase oxidants is a good strategy to overcome the aforementioned disadvantages of gas/ liquid oxidants and afford high efficiency under benign conditions. Peroxymonosulfate (PMS, HSO₅⁻) is a cost-effective oxidant that has been widely applied in the degradation of various contaminants in water.23 It is proven that PMS can be activated by a wide range of catalysts, including supported transition-metals such as Mn, Fe and Co, among which Co affords the best catalytic performance.^{24,25} In most cases, the catalytic activation of PMS will lead to the generation of oxidative radicals ('OH, SO₄^{\cdot} and SO₅^{\cdot}) which play a crucial role in the oxidation of stubborn organic pollutants.²⁶⁻²⁸ Even though PMS receives extensive attention in environmental remediation, its potential application in selective oxidation for fine chemical production is rarely explored.

Herein, we look at a Co-based single atom catalyst anchored on a carbon nitride support with 3.17 wt% Co dopant. To the best of our knowledge, for the first time this has been applied in the selective oxidation of ethylbenzene into acetophenone by PMS activation. The prepared Co SAC exhibited excellent catalytic efficiency as well as reusability, achieving over 97% EB conversion and 95% AcPO selectivity at 60 °C and under atmospheric pressure. The strong C–H bonds in EB molecules were activated by the generated free radicals. This work opens a new route for the fabrication of transition metal based single atom catalysts with their facile application in C–H bond activation under mild conditions.

2. Results and discussion

2.1 Characterization

First, the structure of the prepared samples was systematically studied. As suggested by the XRD results of pure $g-C_3N_4$,



Fig. 1 Characterization of SACo@g-C₃N₄. (a) SEM image of SACo@g-C₃N₄, and the inset shows the optical image of 1.1 g SACo@g-C₃N₄. (b) TEM image and (c) HAADF-STEM image of SACo@g-C₃N₄. (d) HAADF image and the corresponding EDS mapping of SACo@g-C₃N₄, the scale bar is 100 nm. (e) HRTEM image and (f) AC-STEM-annular dark-field (ADF) image of SACo@g-C₃N₄.

SACo@g-C₃N₄ and CoNP@g-C₃N₄ (Fig. S1[†]), the characteristic peaks located at around 13.2 and 27.5° correspond to the inplane structural packing of tri-s-triazine units and the interlayer stacking of aromatic systems, which could be indexed to the (100) and (002) planes of hexagonal g- C_3N_4 (JCPDS 87-1526), respectively. SEM images (Fig. 1a) reveal the graphene-like smooth structure of SACo@g-C₃N₄ different from g-C₃N₄ with an amorphous particle structure as shown in Fig. S2.† The inset image confirms the scalable synthesis of SACo@g-C₃N₄ with a mass of 1.1 g. The mass loading of cobalt was obtained through inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a value of 3.17 wt%. Nitrogen adsorption/desorption isotherms were collected to analyze the surface area of pristine g-C₃N₄, CoNP@g-C₃N₄ and SACo@g-C₃N₄. These results indicate that there is an obvious increase in the specific surface area of SACo@g-C₃N₄ (211 m² g⁻¹) compared with that of g-C₃N₄ (33 m² g⁻¹) and CoNP@g-C₃N₄ (28 $m^2 g^{-1}$) as shown in Fig. S3.[†] Moreover, the TEM image in Fig. 1b indicates the absence of obvious Co particles on SACo@g-C₃N₄, consistent with the XRD results that only carbon plane peaks are observed in SACo@g-C3N4 without the characteristic peaks assigned to Co crystals. Conversely, in the XRD of CoNP@g-C₃N₄, characteristic peaks of Co crystals appeared at $2\theta = 36.6, 42.5, 61.6 \text{ and } 73.9^{\circ}$ corresponding to the (111), (200), (220) and (311) planes (Fig. S1[†]), which fit with the XRD pattern (JCPDS #78-0431). Co nanoparticles are also observed on CoNP@g-C₃N₄ with high resolution TEM (Fig. S4^{\dagger}). EDS elemental mapping demonstrates that the C, N and Co elements are uniformly distributed throughout the SACo@g- C_3N_4 (Fig. 1c and d). In addition, the HRTEM image (Fig. 1e) further confirms that no Co nanoparticles or clusters exist on SACo@g-C3N4. AC-STEM-annular dark-field (ADF) was employed to directly probe the atomic dispersion of individual Co atoms randomly dispersed on the g-C₃N₄ support, benefiting from the higher Z-contrast of Co than that of N and C (Fig. 1f). The structural investigation of SACo@g-C3N4 reveals the successful synthesis of single cobalt atoms embedded in g- C_3N_4 .



Fig. 2 Chemical structure of SACo@g- C_3N_4 . (a and b) Carbon and nitrogen K-edge NEXAFS spectra of $g-C_3N_4$ and SACo@g- C_3N_4 . (c) XANES Co-edge and (d) Fourier transform of the EXAFS spectra of Co₃O₄, CoPc, Co foil and SACo@g- C_3N_4 .

X-ray photoelectron spectroscopy (XPS) was employed to probe the composition and status of the relevant elements. In the C 1s spectrum, the two peaks at 284.6 and 287.9 eV can be assigned to C-C and N-C=N, respectively (Fig. S5b[†]). The N 1s spectrum was fitted into three peaks of C-N=C (398.6 eV), N-C3(400.0 eV) and C-N-H (401.1 eV) (Fig. S5c[†]). Synchrotronbased near-edge X-ray absorption fine structure (NEXAFS) was performed to further investigate the interfacial interaction of g-C₃N₄ and SACo@g-C₃N₄. In the carbon K-edge NEXAFS spectra (Fig. 2a), both g-C₃N₄ and SACo@g-C₃N₄ reveal the presence of characteristic resonances of carbon nitride: π *C=C at 286.2 eV, π *C-N-C at 288.1 eV, and long-range σ *C-C resonance occurring over the range of 292-300 eV.29 In the nitrogen K-edge region (Fig. 2b), g-C₃N₄ and SACo@g-C₃N₄ show two typical π^* resonances at 399.7 (N1) and 402.5 eV (N2) corresponding to the aromatic C-N-C coordination in one tri-striazine heteroring (N1) and the N-3C bridging among three tris-triazine moieties (N2).³⁰ The Co 2p spectrum (Fig. S5d⁺) displays that the Co species in SACo@g-C₃N₄ were composed of Co²⁺ around 780.6 eV, which are indexed to the Co-N species instead of metallic Co(0).31 For a better investigation of the electronic structure and coordination environment of Co in SACo@g-C₃N₄, X-ray absorption near-edge structure (XANES) was further conducted, where the presence of Co K-edge exhibits a similar pre-edge structure to that of CoPc (Fig. 2c). Moreover, the Fourier transforms (FT) obtained from the extended X-ray absorption fine structure (EXAFS) clearly indicated that the dominant peak of SACo@g-C₃N₄ was located at approximately 1.50 Å. This observation is due to the formation of Co-N bonds which are much shorter than the Co-O peak at 1.64 Å in standard Co₃O₄ and far different from the Co-Co peaks at 2.18 Å (Fig. 2d). It is a solid confirmation that the Co species in SACo@g-C3N4 were atomically dispersed and chemically coordinated in the Co-N bonds.

The chemical structures of g-C₃N₄ and SACo@g-C₃N₄ were further investigated through FTIR analysis. Fig. S6[†] presents three main absorption regions in the FTIR spectra of g-C₃N₄ and SACo@g-C₃N₄. The broad peak at 3000–3500 cm⁻¹ is assigned to the stretching vibration of N–H and surface water molecules. The peaks at 1343–1472 cm⁻¹ are ascribed to the characteristic vibration of aromatic rings and the peaks at 1640 cm⁻¹ are mainly due to the presence of C–N bonds.³² The characteristic peaks over 1200–1700 cm⁻¹ in SACo@g-C₃N₄ are weakened compared with those of pure g-C₃N₄, possibly due to the presence of amorphous carbon on the surface of SACo@g-C₃N₄ derived from decomposition of citric acid,³³ consistent with the dark color change shown in Fig. 1a.

2.2 Catalyst evaluation

The selective oxidation of EB over different catalysts by PMS was carried out at 60 °C, which is lower than most of the reported cases with O2 or liquid peroxide oxidants (Table S1⁺). The solvent selection and product analysis methodology were determined according to our reported work.34 Without a catalyst, a very low oxidation efficiency was obtained, affording only 10.8% EB conversion and 7.3% AcPO yield after reaction for 15 h (Table 1, entry 1). Hence the PMS molecules without activation can hardly oxidize the strong C-H bond in EB. The loading of Co-free g-C₃N₄ increased the EB conversion up to 27.4%, which is in accordance with the previous research that the plain g-C₃N₄ has a certain but limited functionality for inducing the PMS activation.24,35 Upon insertion of Co nanoparticles in $g-C_3N_4$ (CoNP@g-C₃N₄), the EB conversion was remarkably improved to 90.6% with an AcPO selectivity of 88.4% (Table 1, entry 3). However, the CoNP@g-C₃N₄ was almost completely deactivated after the reaction, giving merely 14.4% conversion in the second run. Meanwhile, the Co content on the spent CoNP@g-C3N4 dropped to 0.15 wt% in comparison with the 4.50 wt% of the fresh catalyst as detected by ICP-AES. Meanwhile, Co particles can seldom be seen in the SEM/TEM images of used CoNP@g-C3N4 which only had weak Co signals sparsely distributed in the sample as observed by the EDS mapping (Fig. S7[†]). It can be inferred that the Co NPs are highly unstable in PMS solvent as the acidity of the solution was increased with the proceeding of the oxidation reaction; thus

 Table 1
 Selective oxidation of EB on different catalysts^a

Entry	Catalyst	Co (wt%)	EB conversion (%)	Selectivity (%)		AcPO
				1	Blank	_
2	g-C ₃ N ₄	—	27.4	69.6	1.5	19.1
3	CoNP@g-C ₃ N ₄	4.50	90.6	88.4	0.1	80.1
4	CoNP@g-C ₃ N ₄ (used)	0.15	14.4	99.6	0	14.3
5	SACo@g-C ₃ N ₄	3.17	97.5	95.6	0.2	93.2

 a Reaction conditions: 5 mg catalyst, 0.1 mmol EB, 0.5 mmol PMS, 10 mL acetonitrile/water (1 : 1, volume ratio), 60 $^\circ$ C, 15 h.



Fig. 3 (a) Recycling and stability test of SACo@g-C₃N₄ (reaction conditions: 5 mg catalyst, 0.1 mmol EB, 0.5 mmol PMS, 10 mL acetonitrile/water 1 : 1, 60 °C, 24 h). The effects of reaction conditions on the selective oxidation of EB with SACo@g-C₃N₄ (5 mg catalyst, 0.1 mmol EB and 10 mL acetonitrile/water 1 : 1). (b) PMS concentration (60 °C, 15 h). (c) Reaction temperature (0.5 mmol PMS, 15 h). (d) Reaction time (60 °C, 0.5 mmol PMS).

the activity of CoNP@g-C₃N₄ stemmed from the enhanced homogeneous catalysis as a result of the gradually leaching of Co ions. The SACo@g-C₃N₄ achieved an extraordinary oxidation efficiency of 97.5% EB conversion with 95.6% AcPO selectivity and 93.2% AcPO yield, dynamically confirming that Co single atoms are the active sites for the PMS-mediated EB oxidation. Moreover, excellent catalytic stability and reusability were observed for SACo@g-C₃N₄ by conducting 4 recycling tests with each one running for 24 h (Fig. 3a). There is no obvious sign of activity loss within 4 runs and the Co content nearly remained unchanged for SACo@g-C3N4 throughout the oxidation process $(3.12 \text{ wt\% after the 4th run } \nu s. 3.17 \text{ wt\% for the fresh catalyst}),$ demonstrating that the Co single atoms are strongly coordinated to the g-C₃N₄ support with adequate resistance against the long reaction time in this acidic oxidizing solvent. This highlights the advantage of SACo@g-C₃N₄ as a robust catalyst to work in a facile manner for PMS activation without the requirement of pH control and additional buffer. Besides the AcPO formed as the dominant product, a minimal amount of 1phenylethanol (1-PA) was also produced during the EB oxidation. The selectivity of 1-PA was below 1.5% for all the tested catalysts shown in Table 1, and was further reduced below 0.2% for the SACo@g-C3N4 catalyzed EB oxidation regardless of different conditions such as PMS concentration and reaction time. This suggests that the C-H bond activation could directly lead to the formation of ketone derivatives instead of following a consecutive reaction route to yield 1-PA and subsequently AcPO. Overall, the catalytic performance of SACo@g-C3N4 is comparable to the level of the highest EB oxidation efficiency ever reported (Table S1[†]). More specifically, this SACo@g-C₃N₄/ PMS configuration demonstrated superior EB conversion rate and selectivity for AcPO in comparison with the reported oxidations using O2, H2O2 and TBHP as the respective oxidant,

and the current system required a much lower reaction temperature and shorter time.

To understand the influence of oxidant loading, the oxidation efficiency over SACo@g-C₃N₄ as a function of PMS/EB ratio (from 2 to 6) was investigated. As shown in Fig. 3b, the conversion and product yield increased rapidly with higher PMS concentration. Over 90% EB was converted at a PMS/EB ratio of >4, and the EB conversion was >99% when the PMS/EB ratio was 6. Surprisingly, there was no severe loss of AcPO selectivity with higher PMS loading, indicating that both the EB and the AcPO are not likely to be deeply oxidized in PMS solution. The reaction efficiency is also greatly affected by the reaction temperature (Fig. 3c). Increasing the temperature from 30 to 45 °C contributed to a remarkable elevation of EB conversion by 40%, while further increment of temperature to 60 °C was less effective to enhance the oxidation. Therefore, a minor input of energy is necessary to assist the highly efficient PMS activation and to overcome the energy barrier of C-H bond activation. Furthermore, the continuous oxidation reaction with time is displayed in Fig. 3d. The conversion reached 89.1% at 3 h, manifesting that the SACo@g-C3N4/PMS system enables the C-H activation with a high reaction rate. After 3 h of reaction, the conversion continued to increase but the reaction rate decreased and finally climbed up to 98.8% at 24 h. In contrast, the AcPO selectivity slightly reduced with reaction time, but still showed a high selectivity of 93.9% at 24 h. The oxidation efficiency over the SACo@g-C3N4/PMS system under different conditions confirms its excellent catalytic performance, showing large potential in selective oxidation reactions.

2.3 Identification of the oxidation mechanism

Various reactive radicals such as 'OH (1.8-2.7 V), SO4 '- (2.5-3.1 V) and SO_5^{-} (1.1 V) can be generated from the PMS activation via electron-transfer between PMS and the Co catalyst.²⁶ As illustrated in eqn (1)-(5), the continuous decomposition of PMS is accomplished with the redox cycle of $Co(\pi)/Co(\pi)$, thereby forming free radicals. Sulfate radicals usually have a greater impact on the oxidation reaction than other radicals because of their higher redox potential and longer half-life period.³⁶ Apart from that, singlet oxygen and non-radical oxidations by catalystmediated electron transfer are also reported as possible pathways for the PMS enabled oxidation process.37-39 To identify the intrinsic oxidative species responsible for the selective conversion of EB, both electron paramagnetic resonance (EPR) and radical scavenging tests were performed. It is suggested from Fig. 4a that SACo@g-C₃N₄ is superior to the metal-free g-C₃N₄ in generating 'OH radicals. The signals of SO_4 ' radicals are not very distinct, whereas some ambiguous signals appeared between two adjacent signals of 'OH radicals. We assume that this phenomenon could be attributed to the presence of both DMPO-SO₄^{•–} and DMPOX,⁴⁰⁻⁴² an oxidation product of DMPO due to the excessive amount of oxidizing species such as 'OH and SO_4 .

$$HSO_5^- + Co(II) \rightarrow SO_4^{-} + OH^- + Co(III)$$
(1)

$$HSO_5^- + Co(II) \rightarrow OH + SO_4^{2-} + Co(III)$$
(2)



Fig. 4 (a) EPR spectra of $g-C_3N_4$ and SACo@g- C_3N_4 catalyzed PMS activation in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO). (b) The influence of TBA and MeOH concentration on the formation of AcPO over SACo@g- C_3N_4 . (c) Proposed mechanism of SACo@g- C_3N_4 -mediated PMS activation and selective conversion of EB.

$$SO_4^{-} + OH^- \leftrightarrow OH + SO_4^{-}$$
 (3)

$$HSO_5^- + Co(III) \rightarrow SO_5^{-} + H^+ + Co(II)$$
(4)

$$2SO_5^{\cdot -} \rightarrow {}^1O_2 + 2SO_4^{\cdot -} \tag{5}$$

The radical scavenging tests using tert-butanol (TBA) and methanol (MeOH) were then conducted to evaluate the functions of different radicals in C-H activation. MeOH is used as a quencher for both hydroxyl and sulfate radicals owing to its high reactivity towards these two radicals, whereas TBA without α -H shows a much weaker scavenging effect on SO₄⁻⁻ than on 'OH.43 The influence of excess concentration of TBA or MeOH on the reaction efficiency over SACo@g-C3N4 catalyzed EB oxidation is displayed in Fig. 4b and S8.† As expected, the addition of MeOH has a greater effect than TBA on suppressing the EB conversion and AcPO formation. Specifically, at 10 times dose of the quenching agents, 20.1 and 84.8% AcPO yields were attained for MeOH and TBA loaded experiments, respectively, compared with the 93.2% AcPO yield from the no-quenching experiment. The AcPO yield decreased to 0 at a MeOH/PMS ratio of 100, while 32.9% AcPO yield was obtained with the same concentration of TBA. It can be concluded that the activation of C-H in EB originates from the oxidative radicals and the sulfate radicals play the dominant role in the C-H oxidation to fabricate AcPO with high selectivity, as illustrated in Fig. 4c. Considering that the Co atoms in SACo@g-C₃N₄ dominantly exist as Co (π), as mentioned above, the SO₄^{•-} radicals are readily generated via eqn (1)-(3). It is noteworthy that in some

oxidative reactions using Co-based catalysts, the oxidation of the organic substrate by the Co catalyst/PMS system was accomplished *via* both radical and non-radical processes.^{44,45} While in other cases with different organic substrates or supporting materials for Co active sites, the oxidation reaction was dominantly attributed to the sulfate radicals.^{24,28} Thus it follows that the intrinsic mechanism for the PMS-derived oxidation process is closely related to not only the catalyst category (especially the interactions of metal active centers and different supports) but also the adsorptive properties of the organic substrate.

3. Experimental

3.1 Synthesis of g-C₃N₄

The g-C₃N₄ was synthesized by annealing urea in air. First, urea (CON₂H₄, 90 g) was put into a covered alumina crucible and placed inside a muffle furnace. Then, the temperature was increased up to 600 °C (ramp rate 10 °C min⁻¹) and held for 2 h. Finally, around 7 g of g-C₃N₄ was collected. For safety, the annealing process was carried out in a fume cupboard to ventilate the produced smoke. Before usage, the g-C₃N₄ was further ground for 20 min to get a uniform yellowish powder.

3.2 Synthesis of SACo@g-C₃N₄

The SACo@g- C_3N_4 (Co single atom doped g- C_3N_4) was synthesized as follows. First, citric acid (C₆H₈O₇, 2 g) was added to a mixed solution of isopropanol and acetone (volume ratio of 2:1, 100 mL). After stirring for 10 min, a transparent solution was obtained followed by the addition of cobalt(II) phthalocyanine (CoPc, 100 mg). The violet solution was stirred for 2 h and the fine ground $g-C_3N_4$ powder (5 g) was added to the above solution. The mixture was stirred and naturally evaporated to 10 mL volume. Then, the whole mixture was transferred into an agate mortar and ground to dry powder. The yellow powder was heated to 655 °C at a ramp rate of 7 °C min⁻¹ and kept for 2 h under Ar at a flow rate of 50 mL min⁻¹. The obtained black powder was dispersed in excess oxone (peroxymonosulfate) solution (20 g L^{-1}) and stirred at 50 °C for 24 h, and then thoroughly washed and dried at 60 °C overnight. The final black powder was denoted as SACo@g-C3N4.

3.3 Synthesis of CoNP@g-C₃N₄

Cobalt(II) acetylacetonate ($C_{10}H_{16}CoO_4$, 50 mg) and g- C_3N_4 powder (200 mg) were first ultrasonicated for 10 min and dispersed in 30 mL of ethanol and then transferred into 100 mL of ethylene glycol solution. The dispersion was stirred for 1 h before being placed in a lab-use microwave oven (1000 W) in a fume cupboard and heated for 5 min. The solution was then filtered using a membrane film and washed with ethanol 5 times. The final yellowish powder was dried in an oven at 80 °C for 5 h and was denoted as CoNP(a)g-C₃N₄.

3.4 Selective oxidation of ethylbenzene

In a typical EB oxidation reaction, 5 mg of catalyst was added to 10 mL of acetonitrile/water 1 : 1 solvent in a three-necked flask

and the mixture was sonicated for a few minutes to fully disperse the catalyst. The reaction started with the addition of 0.1 mmol of EB and 0.5 mmol of oxone (KHSO₅·1/2KHSO₄·1/ 2K₂SO₄) and was maintained at 60 °C for 15 h in an oil bath. Then the flask was naturally cooled down for around 2 min, followed by the addition of 0.1 mmol of anisole as the internal standard. The catalyst was filtered out and the aromatic compounds were extracted from the reaction solution using toluene for three times (the volume usage of toluene and the reaction solution is 6:1), and the organic phase was analyzed by gas chromatography (GC). The reactions performed under other conditions were achieved with the same procedure except that the relevant parameters were adjusted as required. The radicals generated during the oxidation reaction were probed by electron paramagnetic resonance (EPR) on a Bruker EMS-plus instrument. The EPR data were analyzed with Xeon software using 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 0.08 M) as the spin-trapping agent.

4. Conclusions

In this study, we demonstrated a novel approach to the synthesis of cobalt-based catalysts with individually dispersed Co atoms doped on g-C₃N₄. Joint characterization proofs verify that the anchored Co atoms (3.17 wt%) were coordinated with N species to form highly stable Co-N bonds. The maximized utility efficiency of Co and the outstanding stability of such a robust catalyst can be utilized for the activation of the C-H bond in EB by PMS, achieving a 93.2% yield of AcPO at a low temperature of 60 °C. The selective conversion of EB into AcPO relies on the rapid generation of free radicals from activated PMS, along with the redox cycle of $Co(\pi)/Co(\pi)$. Sulfate radicals, with a higher oxidation potential, play a more significant role than other radicals to activate the inert C-H bonds. This work presented a novel synthesis strategy of a Co-based single-atom catalyst that could be expanded to prepare SACs of other transition-metals. More importantly, the developed SAC displays a promising efficiency for selective oxidation of ethylbenzene to acetophenone by PMS activation, which opens a new way for breaking C-H bonds in various hydrocarbons for organic synthesis.

Conflicts of interest

There are no conflicts to declare.

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