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Cobalt single atoms anchored on nitrogen-doped porous carbon as an efficient catalyst for oxidation of silanes[†]

Fan Yang,‡ Zhihui Liu,‡ Xiaodong Liu, Andong Feng, Bing Zhang, Wang Yang and Yongfeng Li *

The oxidation reactions of organic compounds are important transformations for the fine and bulk chemical industry. However, they usually involve the use of noble metal catalysts and suffer from toxic or environmental issues. Here, an efficient, environmentally friendly, and atomically dispersed Co catalyst (Co-N-C) was prepared via a simple, porous MgO template and etching method using 1,10-phenanthroline as C and N sources, and CoCl₂·6H₂O as the metal source. The obtained Co-N-C catalyst exhibits excellent catalytic performance for the oxidation of silanes with 97% isolated yield of organosilanol under mild conditions (room temperature, H₂O as an oxidant, 1.8 h), and good stability with 95% isolated vield after nine consecutive reactions. The turnover frequency (TOF) is as high as 381 h^{-1} , exceeding those of most non-noble metal catalysts and some noble metal catalysts. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), extended X-ray absorption fine structure (EXAFS), and wavelet transform (WT) spectroscopy corroborate the existence of atomically dispersed Co. The coordination numbers of Co affected by the pyrolysis temperature in Co-N-C-700, Co-N-C-800, and Co-N-C-900 are 4.1, 3.6, and 2.2, respectively. Owing to a higher Co-N₃ content, Co-N-C-800 shows more outstanding catalytic performance than Co-N-C-700 and Co-N-C-800. Moreover, density functional theory (DFT) calculations reveal that the $Co-N_3$ structure exhibits more activity compared with $Co-N_4$ and $Co-N_2$, which is because the Co atom in $Co-N_3$ was bound with both H atom and Si atom, and it induced the longest Si-H bond.

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1. Introduction

The green oxidation reaction of organic compounds, such as silanes, is among the most important transformations in organic synthesis to build up key intermediates for the synthesis of the agrochemical, pharmaceutical, and other fine chemicals.¹ Although organosilanes can produce the corresponding products under the action of strong oxidants, such as dioxiranes,² osmium tetroxide,³ ozone,⁴ and oxaziridines,⁵ chemo-selective oxidation of silanes is a great challenge because of the condensation or the decomposition of silanol. Recently, great efforts have been devoted to developing heterogeneous catalysis for the oxidation of silanes to silanols, which represents an eco-friendly approach based on the use of oxygen, water, or hydrogen peroxide as the oxidant. Despite its

green and atom-economical feature, most of the studies were focused on noble metals, which serve as the catalytic centre of silane oxidations, such as Au,⁶ Pd,⁷ Pt,⁸ Ag,⁹ Ir,¹⁰ and Ru.¹¹ Although most noble metal catalysts show excellent activity, the limited supply and high cost of precious metals restrict their sustainable development. Non-noble metal catalysts $Mn(ClO_4)_2 \cdot 6H_2O_{,}^{12} \quad Cu_3(BTC)_{2},^{13}$ including nanoporous copper,¹⁴ NaY zeolite,¹⁵ and Ni powder^{1a} have received great consideration for silane oxidations due to their relatively abundant reserves and low cost. However, non-noble metal catalysts often require more stringent reaction conditions, and they show poor catalytic performance. Therefore, it is desirable to search for more economical, efficient, and eco-friendly alternatives to catalyse the oxidation of organosilane.

Single-atom catalysts (SACs) are emerging as a new frontier in heterogeneous catalysis due to their excellent catalytic performance.¹⁶ As one of the most remarkable noble-metal-free SACs, M–N–C catalysts (M = Ni, Fe, Co) have been widely investigated for a wide range of applications, including organic molecular transformation reactions,¹⁷ electrochemical oxygen reduction reaction (ORR),¹⁸ CO₂ reduction,¹⁹ hydrogenation,²⁰

State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), Beijing 102249, China. E-mail: yfli@cup.edu.cn

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[‡]These authors contributed equally.

CO oxidation,²¹ proton exchange membrane fuel cells,²² and other chemical processes²³ due to their unique advantages including maximum metal utilization, good recyclability, and unique electronic structure. Moreover, Co-N-C catalysts with excellent performance have attracted wide attention as a catalyst in organic oxidation reactions such as peroxymonosulfate oxidation,²⁴ oxidative esterification of furfural,²⁵ ethylbenzene oxidation,²⁶ Wacker-type oxidation,²⁷ oxidative cleavage of 1,2diols,²⁸ oxidative esterification of primary alcohols,²⁹ sulfide oxidation,³⁰ and oxidative dehydration of N-heterocycles.³¹ We speculate that the Co-N-C catalyst has such good oxidation performance due to the unique electronic structure among cobalt, nitrogen, and carbon. Therefore, it is highly desirable to develop a SAC Co-N-C catalyst with high efficiency for the oxidation of organosilanes to organosilanols under mild conditions.

Herein, we report a facile approach to synthesize SAC Co-N-C catalysts *via* the one-step pyrolysis of cobalt-phenanthroline complexes on porous MgO sheets and acid leaching. Owing to its unique structure, Co-N-C catalysts exhibit excellent catalytic activity for the oxidation of organosilanes. Notably, the catalyst is very easily recycled, which can be conveniently reused ten times. HAADF-STEM and EXAFS spectroscopy were used to reveal the existence of atomically dispersed Co and its coordination number with the N atom in synthesized catalysts. The controlled trials and DFT are carried out to identify the active sites and understand the reaction mechanism of the catalysts for the oxidation of organosilanes. Moreover, Co-N-C catalysts also show excellent catalytic activity in the oxidative esterification of alcohols.

2. Materials and methods

2.1. Materials

All chemicals and solvents were purchased from commercial suppliers without further purification: magnesium oxide (Sinopharm Chemical Reagent Co., Ltd); triphenylmethane, iron(II) oxalate dihydrate (Aladdin Industrial Corporation); palladium acetate (Wako Pure Chemical Industries, Ltd); 1-butyl-3-methylimidazolium-tetrafluoroborate and cuprous iodide (Tokyo Chemical Co., Ltd); nitrobenzene, 4-nitroanisole, 4-nitrotoluene, and cesium fluoride (Sinopharm Chemical Reagent Co., Ltd); 8-nitroquinoline and benzoxazole (Sun Chemical Technology (Shanghai) Co., Ltd); 1,3-dinitrobenzene, p-nitrobenzoic acid, o-nitrobenzoic acid, and methyl 4-nitrobenzoate (Xiya Chemical Industry Co., Ltd); 4-nitrobenzonitrile, p-nitroacetophenone, iodobenzene, p-nitrophenol, o-nitrophenol, silver oxide, and phenylacetylene (J&K Scientific Co., Ltd); acetone, ethanol, hydrogen peroxide, tetrahydrofuran, sulfuric acid, and magnesium sulphate (Beijing Chemical Works).

2.2. Preparation of the MgO template

Porous layer MgO was prepared according to the previously reported literature.³² First, the purchased MgO powder (30 g) was mixed with deionized water (300 mL) followed by ultra-

sonic agitation. The mixture was boiled for 24 hours in a reflux apparatus. After filtration and drying, the material obtained was ground into a fine powder. Finally, the powder was calcined at 550 $^{\circ}$ C for one hour to remove water.

2.3. Synthesis of cobalt/nitrogen-doped porous carbon hybrids

The typical procedure for the preparation of the catalysts is described as follows: a mixture of CoCl₂·6H₂O (475.8 mg, 2 mmol) and 1,10-phenanthroline (720.8 mg, 4 mmol) in ethanol (200 mL) was stirred for 30 minutes at room temperature. Then, porous MgO layers (2 g) were added, and the whole reaction mixture was stirred at 60 °C for 2 hours. The reaction mixture was cooled to room temperature, and ethanol was removed by rotary evaporation. The remaining solid sample was ground into a powder, and then pyrolyzed at 800 °C for 2 hours under an argon atmosphere. After cooling to room temperature, the obtained black powder (labelled as Co-N-C-MgO) was washed with 5 mol L^{-1} hydrochloric acid with reflux for 30 minutes and 2 mol L⁻¹ H₂SO₄ at 80 °C for 6 h, followed by thorough washing with deionized water. Synthesis processes at different calcination temperatures (700, 800, and 900 °C) were performed, and the products were annotated as Co-N-C-700, Co-N-C-800, and Co-N-C-900, respectively. For comparison, nitrogen-doped porous carbon (labeled as NPC) was prepared was synthesized by a similar process except for the absence of CoCl₂·6H₂O, and cobalt/porous carbon hybrids (labeled as Co-PC) using phenanthrene as the carbon source.

2.4. Synthesis of Co-nanoparticle decorated nitrogen-doped carbon

Co nanoparticles decorated nitrogen-doped carbon (Co NC) were synthesized according to the preparation method of Ni NC by our research group.³³ Firstly, 3 g triphenylmethane and 5 g MgO template were mixed in ethanol solution under magnetic stirring at room temperature. The obtained composite was pyrolyzed at 800 °C for 2 h under an argon atmosphere. After cooling to room temperature, porous carbon was obtained after removal of the MgO template with hydrochloric acid. Then, 160 mg porous carbon was dispersed in ethanol by ultrasonication, followed by the addition of 80 mg of $CoCl_2 \cdot 6H_2O$. After ethanol was removed, the dried product was ground with 400 mg of melamine, followed by pyrolysis at 800 °C for 2 h under an argon atmosphere. The Co NC was synthesized by cooling to room temperature.

2.5. Procedure for the oxidation of organosilanes

In a typical catalysis reaction, 2 mg Co–N–C catalyst, 2 ml acetone, H_2O (108 µL), and dimethylphenylsilane (DMPS) (92 µL, 0.6 mmol) were added in a glass microreactor at room temperature under magnetic stirring. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was filtered off and washed thoroughly with ethyl acetate and acetone. Afterward, the dried catalyst was reused for the next cycle. The solvent from the filtrate was evaporated, and the product was purified in a silica

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column using petroleum ether (60–90 $^{\circ}$ C) as the eluent. Besides, the recyclability of the Co–N–C-800 catalyst was further evaluated in the oxidation of DMPS with twice the amount of catalyst (4 mg).

2.6. Procedure for the oxidation of alcohols to esters

The Co–N–C-800 catalyst (10 mg), K_2CO_3 (11.1 mg, 0.1 mmol), methanol (3 mL), and benzylic alcohol (0.4 mmol) were mixed in a micro reaction vial. The reaction was stirred under 1 bar of oxygen at 60 °C for 12 h, and the reaction process was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature diluted with ethyl acetate. Then, the catalyst was filtered off through a short silica column with ethyl acetate to remove the catalyst, and the product was purified with a silica column using ethyl acetate/ petroleum ether (60–90 °C) as the eluent.

2.7. DFT computational details

Density functional theory (DFT) calculation was performed by the DMol³ code of Materials Studio. The generalized gradient approximation of the revised-Perdew-Burke–Ernzerhof (GGA-RPBE) function, and DFT-D³ dispersion correction by Grimme were used to treat all energy changes.³⁴ The core treatment was the effective core potential (ECP), and the basis set was DNP v4.4. The *k*-point was set as $1 \times 1 \times 1$, and the size of the vacuum region was 20 Å.³⁵ The detailed calculation parameters were reported in our previous studies.³⁶ The typical $Co-N_x-C_y$ (x = 2-4) substrates were modified by a 5×5 super cell of graphene, and all atoms were relaxed.³⁷ The adsorption energy of DMPS on different surfaces was defined by eqn (1).

$$E_{\rm ads} = E_{\rm cal+mol} - E_{\rm mol} \tag{1}$$

where $E_{\text{cat+mol}}$ is the energy of adsorbed molecule on catalyst surface, E_{cat} is the energy of the bare catalyst surface, and E_{mol} is the energy of the molecule in the gas phase. To locate the transition state of a certain reaction, the complete linear synchronous transit (LST)/quadratic synchronous transit (QST) method was applied, the RMS convergence was below 4.0 × 10^{-3} Ha Å⁻¹. Then the intrinsic reaction path (IRP) was confirmed by the nudged elastic band (NEB) method.³⁸

2.8. Characterization

The morphology of the catalyst was characterized using a Hitachi SU8010 scanning electron microscope (SEM) operated at 3.0 kV and a transmission electron microscopy (TEM, Tecnai G2, F20). The aberration-corrected scanning TEM image was taken using a Titan Cubed Themis G2 300 equipped with a spherical aberration corrector. The crystalline phase of the catalysts was identified by X-ray diffraction (XRD) on a Rigaku D/ Max 2500 X-ray diffractometer with Cu K α radiation (18 kW). Raman spectra were recorded with a Renishaw inVia confocal Raman microscope system using green (532 nm) laser excitation. The elemental composition of samples was obtained by X-ray photoelectron spectroscopy (XPS) with an ESCA Lab220i-XL electron spectrometer from VG Scientific using 300 WAl K α

radiation. The Brunauer-Emmett-Teller (BET) surface area measurement was characterized by nitrogen adsorption at 77 K using an SSA-4200 Surface Area and Pore Size analyzer (Beijing Builder Electronic Technology Co., Ltd) instrument. The leaching of Co in consecutive cycles was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). ¹H NMR spectra were recorded on a JNM-LA300FT-NMR for examining the final product of the oxidation of silanes and alcohols. The X-ray absorption fine structure spectra (Co K-edge) were collected using a 1 W1B station in Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF were operated at 2.5 GeV with a maximum current of 250 mA. Using a Si (111) double-crystal monochromator, data collection was carried out in the transmission mode using an ionization chamber. All spectra were collected under ambient conditions. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k^3 -weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k^3 -weighted $\chi(k)$ data of Co K-edge were Fourier transformed to real (R) space using a hanging window (dk =1.0 $Å^{-1}$) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around the central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of the IFEFFIT software packages.

3. Results and discussion

3.1. Catalyst characterization

The Co–N–C catalysts were facilely prepared *via* thermal pyrolysis of carbon, nitrogen, and Co containing complex precursors (Co(Phen)₂Cl₂) using porous MgO as a template. The pyrolysis temperatures are 700, 800, and 900 °C, corresponding to the products labelled as Co–N–C-700, Co–N–C-800, and Co–N–C-900, respectively. And Co–N–C catalysts were finally obtained after the removal of the porous MgO templates and Co particles by acid leaching (Scheme 1). The morphologies of Co–N–C-800 were first characterized by SEM and TEM images. Fig. 1a shows a laminar structure appearance, which is attributed to the thin MgO sheets. In Fig. 1b and c, no cobalt-contain-



Scheme 1 The synthesis process of cobalt/nitrogen-doped porous carbon hybrids.



Fig. 1 (a) SEM image, (b) TEM image, (c) high-resolution TEM image, (d) aberration-corrected HAADF-STEM image, single atoms are highlighted by red circles of Co–N–C-800. (e) TEM image and (f) enlarged image with EDX maps, C (red), N (orange), Co (green) of Co–N–C-800.

ing nanoparticles but amorphous carbon layers in a highly porous structure with nanopores of 3-15 nm were clearly observed in Co-N-C-800. To provide information at an atomic scale, subångström-resolution HAADF-STEM technique was used to inspect the Co-N-C-800 (Fig. 1d), which shows that a large amount of uniformly dispersed Co single atoms is clearly observed. The energy-dispersive X-ray spectroscopy (EDX) elemental mapping shows that the Co species were detected along with C and N elements all homogeneously distributed throughout the whole area of the porous carbon (Fig. 1e and f). Moreover, compared with the commonly used carbon supports,³⁹ the use of the porous MgO presents outstanding advantages of preventing the aggregation of cobalt.⁴⁰ For comparison, NPC, Co-PC, and Co NC samples were also prepared by a similar procedure. These control samples (Co-N-C-700, Co-N-C-900, NPC, Co-PC, and Co NC) show similar morphologies as Co-N-C-800 (Fig. S1-S3[†]). Fig. S3[†] shows that Co nanoparticles are uniformly dispersed on the Co NC surface.

The N2 adsorption-desorption isotherms of the Co-N-C-700, Co-N-C-800, Co-N-C-900, NPC, and Co-PC catalysts show a typical type IV isotherm with a hysteresis loop, indicating the existence of abundant porous structure (Fig. 2a, b and Fig. S4[†]). In good agreement with the TEM result, the Co-N-C-800 samples possess a wide pore size of 2-85 nm. Moreover, N2 adsorption-desorption measurements reveal that Co-N-C-700, Co-N-C-800, and Co-N-C-900 catalysts exhibit mesoporous structural features with high surface areas of 716, 625, and 468 m^2 g⁻¹, respectively. The reduction of the specific surface area may be due to the fact that the pores of the catalyst are damaged to a certain extent at high temperature. And the 3D reconstruction videos of the Co-N-C-800 catalyst are shown in the ESI (Movies S1 and S2[†]). Such a porous morphology, providing a high BET specific surface could maximize the exposure of active sites and enhance the mass transfer and adsorption of reactant, which is desired for catalysis.⁴¹ Further insights into the structural properties are obtained from XRD



Fig. 2 Nitrogen sorption isotherms (a) and pore size distribution (b) of Co-N-C-700, Co-N-C-800, and Co-N-C-900. XRD patterns (c) and Raman spectra (d) of Co-N-C-700, Co-N-C-800, Co-N-C-900, NPC, and Co-PC.

characterization as shown in Fig. 2c and Fig. S5.† The pronounced diffraction peaks at 26.5°, 42.3°, 42.9°, 62.2°, 74.7°, and 78.6° are ascribed to the reflections of C (002), C (100), MgO (200), MgO (220), MgO (311), and MgO (222), respectively. The diffraction peaks at 44.2°, 51.5°, and 75.8° in Co-N-C-MgO can be assigned to the (111), (200), and (220) planes of the Co nanocrystal (PDF 15-0806), respectively. Besides, the diffraction peak at 36.9° can be ascribed to the (311) planes of the Co₃O₄ nanocrystal (JCPDS 43-1003). These results demonstrated that the Co and Co3O4 nanocrystals were formed by the pyrolysis procedure. However, no diffraction peaks of Co, Co₃O₄, and MgO can be observed in Co-N-C catalysts, NPC, and Co-PC, implying that the Co, Co₃O₄ nanocrystals, and MgO component are completely removed during acid leaching. These results illustrate that N was important for the stabilization of a single Co atom. To further estimate the graphitization degree of these carbon materials, Raman spectra of the as-prepared porous carbons are recorded (Fig. 2d). Two conspicuous peaks at about 1353 cm⁻¹ can be assigned to the D band for disordered carbon and defects, and 1589 cm⁻¹ is regarded as the G band for E_{2g} vibrational mode present in the sp²-bonded graphitic carbon. The intensity ratio of the D band to G band (I_D/I_G) is a significant parameter reflecting the defect and disorder degree of graphene. The increased I_D/I_G intensity ratios of Co-N-C-800, Co-N-C-900, NPC, and Co-PC catalysts are observed, and among them Co-N-C-800 and Co-N-C-700 exhibit the highest value of $I_{\rm D}/I_{\rm G}$, indicating that more defective sites or disorders are introduced by Co and N atoms into the carbon network.

XPS measurements are further carried out to probe the chemical compositions and contents of the materials. The XPS spectra of Co–N–C-700, Co–N–C-800, and Co–N–C-900 clearly reveal the presence of C, O, N, and Co elements (Fig. 3a), and



Fig. 3 XPS spectra (a) of Co-N-C-800, Co-N-C-900, NPC, and Co-PC, and the C 1s spectra (b), high resolution N 1s XPS spectrum (c), and Co 2p XPS spectrum (d) of Co-N-C-800. XANES spectra at the Co K-edge (e), Fourier transform (FT) k^3 -weighted $\chi(k)$ -function of the EXAFS spectra (f) and the wavelet transform EXAFS plots (g) of Co-N-C-700, Co-N-C-800, Co-N-C-900, CoPC, and Co foil.

the peaks of C 1s, N 1s, and O 1s are at 283.8, 398.0, 530.7, 779.6, and 795.6 eV, respectively.42 Generally, the C 1s spectrum of Co-N-C-800 in Fig. 3b shows four peaks with binding energies of 284.6, 285.0, 286.1, and 288.2 eV, which can be assigned to the graphitic C, C-N, C=O, and O=C-O, respectively. This result illustrates that N was successfully doped into the carbon materials. The high-resolution N 1s spectra of Co-N-C-800 can be deconvoluted into five different peaks with binding energies of 397.9, 398.4, 399.2, 400.5, and 404.4 eV, corresponding to pyridinic N, Co-N, pyrrolic N, graphitic N, and oxidized N (Fig. 3c), respectively.²⁵ Table S1[†] outlines the atomic surface concentrations, and high N content determined by XPS of Co-N-C-700, Co-N-C-800, and Co-N-C-900 are 8.24, 8.46, and 6.71 at%, respectively. The Co content in Co-N-C-700, Co-N-C-800, and Co-N-C-900 are 2.1, 2.5, and 2.1 wt%, respectively. The amount of Co is high in Co-N-C catalysts owing to the fact that a high nitrogen content helps anchor more cobalt atoms.43 The contents of Co-N are decreased with the increase in temperature (Fig. 3c, Fig. S6, and Table S2[†]), indicating that some Co-N bonds were broken at high temperature. The Co 2p spectrum of Co-N-C-800 exhibits two peaks at 780.0 and 795.5 eV, corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively (Fig. 3d). The binding energy at 780.0 eV and satellite peaks at 783.8 and 801.9 eV are characteristics of Co₂⁺ species coordinating with N atoms in the graphitic layer.⁴⁴ The X-ray absorption spectroscopy (XAS) measurements, containing EXAFS and X-ray absorption near-edge structure (XANES), were performed to further understand the local atomic coordination and electronic structure of the Co species at the atomic level. Co-N-C-700, Co-N-C-800, and Co-N-C-900 show similar

XANES results to cobalt phthalocyanine (CoPC) with a small difference in the edge peaks located at 7710-7716 eV, which are regarded as the fingerprint of Co-N₄ square-planar structures, resulting from a 1s to 4p electron transition (Fig. 3e).45 The Fourier-transformed k^3 -weighted EXAFS spectra (Fig. 3f) displays one main peak at 1.5 Å, corresponding to the Co-N/O first coordination shell, and no Co-Co coordination peak at 2.2 Å can be detected.⁴⁶ These messages mean that no Co particles exist in as-synthesized catalysts, and the CoN_x structure is integrated into the carbon frameworks. Owing to the forceful resolution in K and R spaces, WT was used to study the atomic configuration of Co-N-C samples (Fig. 3g). The WT plots in Co-N-C shows the maximum peak at 4 Å⁻¹, corresponding to the Co-N coordination by contrasting with Co foil and CoPc. In addition, no intensity maximum at 8 $Å^{-1}$ corresponding to Co-Co coordination can be observed. These results further illustrate the isolated feature of Co species in Co-N-C-700, Co-N-C-800, and Co-N-C-900 catalysts. The quantitative EXAFS fitting results reveal that the coordination numbers of Co in Co-N-C-700, Co-N-C-800, and Co-N-C-900 are 4.1, 3.6, and 2.2 (Fig. S7 and Table S3[†]), respectively, and reduction of the number with temperature increase due to the destruction of Co-N at high temperatures,^{19a} which neatly supports XPS results. These results demonstrate the homogeneous dispersion of Co throughout the whole material. Such finely dispersed Co species coordinate with the N atoms to form Co-N moieties, which are highly beneficial for the catalysis of organic transformations.

3.2. Catalytic performance

We used Co–N–C catalysts for the oxidation of organosilanes to organosilanols, and the results are summarized in Table 1. The catalysis of 0.6 mmol of DMPS with 6 mmol H_2O in different solvents, such as acetone, ethyl acetate, tetrahydrofuran, and H_2O , using 2 mg Co–N–C-800 was initially performed at room temperature. The catalytic activity of Co–N–

Table 1 The oxidation of organosilanes under different conditions^a

Catalyst	Solvent	Time (h)	Yield ^d (%)
Co-N-C-800	Acetone	1.8	97
Co-N-C-800	Ethyl acetate	2.1	96
Co-N-C-800	THF	7.8	94
Co-N-C-800	H_2O	25	82
NPC	Acetone	2	7
$NPC + CoCl_2 \cdot 6H_2O$	Acetone	3	20
Co-PC	Acetone	2	0
$L + CoCl_2 \cdot 6H_2O$	Acetone	3	9
Co NC	Acetone	3	22
Co-N-C-700	Acetone	1.8	84
Co-N-C-900	Acetone	1.8	80
	$\begin{array}{c c} & & & \\ \hline & & \\ \hline & & \\ \hline & \\ \hline \\ Catalyst \\ \hline \\ Co-N-C-800 \\ Co-N-C-800 \\ Co-N-C-800 \\ Co-N-C-800 \\ OC-N-C-800 \\ NPC \\ NPC + CoCl_2 \cdot 6H_2O \\ Co-PC \\ L + CoCl_2 \cdot 6H_2O \\ Co NC \\ Co-N-C-700 \\ Co-N-C-700 \\ Co-N-C-900 \\ \hline \end{array}$	$\begin{tabular}{ c c c c } \hline Catalyst & + H_2O & \hline \hline room temperature & O \\ \hline Co-N-C-800 & Acetone \\ \hline Co-N-C-800 & H_2O \\ \hline NPC & Acetone \\ \hline Co-N-C-800 & H_2O \\ \hline NPC & Acetone \\ \hline Co-N-C-800 & Acetone \\ \hline Co-PC & Acetone \\ \hline Co-PC & Acetone \\ \hline Co-N-C-700 & Acetone \\ \hline Co-N-C-900 & Acetone \\ \hline \end{tabular}$	$\begin{array}{c c} \begin{array}{c} \begin{array}{c} \ \ \ \ \ \ \ \ \ \ \ \ \ $

^{*a*} Reaction conditions: Silanes (0.6 mmol), cat. Co–N–C-800 (2 mg), and H₂O (108 μL) in 2 mL solvent. ^{*b*} NPC (2 mg), CoCl₂·6H₂O (1.5 mg). ^{*c*} L = 1,10-phenanthroline. L (1.8 mg), CoCl₂·6H₂O (1.2 mg). ^{*d*} Isolated yield.

C-800 decreased in different solvents in the following order: acetone > ethyl acetate > tetrahydrofuran (THF) > water. Among the above solvents, acetone proved to be the best reaction medium mainly because it shows good performance to well dissolve reactants and provides a highly dispersed system for the Co-N-C-800 catalyst. Ethyl acetate and THF show inferior performance, which is possibly because the water solubility and catalyst dispersibility are a little bit lower than acetone. The worst catalytic activity of the oxidation of DMPS in water perhaps owing to poor dispersibility performance of the Co-N-C-800 catalyst in water and the immiscibility of the DMPS with water (entries 1-4).^{10b,14} For identifying the active species of the catalyst, a series of control experiments, using NPC, NPC and CoCl₂·6H₂O; Co-PC, 1,10-phenanthroline and CoCl₂·6H₂O; Co-N-C-700; and Co-N-C-900 as catalysts were carried out. NPC, NPC and CoCl₂·6H₂O; Co-PC, 1,10-phenanthroline and CoCl₂·6H₂O; and Co NC showed extremely low activities, affording methyldiphenylsilanol in 7%, 20%, 0%, 9%, and 22% respectively (entries 5-9). It is demonstrated that the N doped carbon, the Co salt, and Co nanoparticles contribute little to this reaction. Co-N-C-700 and Co-N-C-900 show a lower performance than Co-N-C-800, giving methyldiphenylsilanol in 84% and 80%, respectively (entries 10 and 11). Based on the control experiments and characterization results, it can be concluded that the Co single atoms bonded to N atoms in the graphitic sheets play a vital role in the overall catalytic performances. It is possible that the Co-N₃ species show better activation performance than Co-N2 and Co-N₄ owing to the fact that the higher content of Co-N₃ exists in Co-N-C-800 compared with that in Co-N-C-700 and Co-N-C-900. In addition, the gram-scale reaction also shows an excellent catalytic effect within 3 h, which indicates that our catalyst has the potential for large-scale application (Scheme 2).

In view of sustainable development, we further explored the generality of the oxidation of organosilanes in acetone by using Co–N–C-800 as a catalyst (Table 2). Satisfyingly, the oxidation of phenyl substituted silanes, such as triphenylsilane and methyldiphenylsilane, giving triphenylsilanol and methyldiphenylsilane in good to high yield (entries 1 and 2). Unfortunately, we discover that the catalyst exhibits an inferior reactivity for the hydrolytic oxidation of aliphatic silanes (entry 3), which was also observed in some reported noble metal-based catalysts.¹⁵ Noteworthily, the oxidation of DMPS with alcohols in the corresponding alcohol solution were also performed, producing the corresponding silyl ethers in high yields (entries 4–6).

We also compared the efficiency of Co-N-C-800 with that of the ever-reported catalysts in the literature (Table S4[†]).





Table 2 Co-N-C-800 catalyzed the oxidation of organosilanes^a



^{*a*} Reaction conditions: 0.6 mmol silanes, 108 μL H₂O in 2 mL acetone, 2 mg Co–N–C-800 catalyst, room temperature. Isolated yield. ^{*b*} Reaction conditions: 0.6 mmol silanes, 1 mL methanol, 2 mg Co–N–C-800 catalyst, room temperature. ^{*c*} Reaction conditions: 0.6 mmol silanes, 1 mL ethanol, 2 mg Co–N–C-800 catalyst, room temperature. ^{*d*} Reaction conditions: 0.6 mmol silanes, 1 mL isopropanol, 2 mg Co–N–C-800 catalyst, room temperature.

Although the turnover frequency (TOF) value of the catalyst calculated from the oxidation of organosilanes to organosilanols (381 h⁻¹ based on the total amount of Co species) is lower than that of precious metal single-site Au catalyst and Pd nanocatalyst (Pd/XC-72-700-Ar) (entries 2 and 3), Co–N–C-800 is prepared by a facile one-step calcination. Impressively, Co– N–C-800 shows better catalytic activity than some noble–metal catalysts (Pd/MgO catalyst and Au nanoparticles) (entries 4 and 5) and other heterogeneous catalysts (Cu₃(BTC)₂, nanoporous copper, NaY zeolite, and Ni powder) (entries 6–9) under comparative reaction conditions. Compared with homogeneous catalysts (TC-6, Mn(ClO₄)₂·6H₂O, and lacunary polyoxotungstate), it also exhibits comparative catalytic activity under comparative reaction conditions (entries 10–12). In short, Co–N– C-800 delivers superior performance in the oxidation of PMDS.

Moreover, the recyclability of the Co–N–C-800 catalyst is further examined in the oxidation of DMPS. After the reaction, the catalyst was filtered off and washed thoroughly with ethyl acetate and acetone for the next run. The isolated yield obtained from each run is shown in Fig. 4a. Although the chemical selectivity remains great all the time, more time is needed to maintain the good yield of dimethylphenylsilanol. We found that the yield of dimethylphenylsilanol remained



Fig. 4 The yields and reaction times for 10 cycles of the Co-N-C-800 catalyzed oxidation of DMPS (a) and TEM image (b) of Co-N-C-800 after 10 cycles.

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 \sim 95% in 13 h after the fifth cycle. This is probably because the adhesion of some organic substances on the catalyst surface prevented the active center from coming in contact with DMPS. However, the Co-N-C-800 catalyst can be reused ten times without obvious deactivation. These results illustrate that the Co-N-C-800 catalyst exhibits good catalytic activity and recyclability. To analyse the reason for the inactivation of the catalyst and confirm that the reaction was indeed catalyzed by solid Co-N-C rather than by homogeneous Co species, the leaching test was performed. After the catalytic oxidation of DMPS was carried out for 1 h under standard conditions, the catalyst was removed from the vessel by filtering with the product produced in 56% yield at this time (Fig. S8[†]). No further reaction took place after removing the catalyst from the reaction mixture. After the reaction, 1.53 ppm of Co was detected in the reaction supernatant, which was confirmed by ICP-OES. Thus, these results illustrate that leaching Co cannot catalyse the oxidation of the DMPS reaction, and the decreased activity of the Co-N-C-800 catalyst is primarily due to metal leaching during the recycle reactions. In addition, the Co-N-C-800 catalyst after cycling test has also been examined by TEM (Fig. 4b), and the morphology of the recycled catalyst does not change.

Eventually, to extend the applications of the catalyst, we further use the Co–N–C-800 catalyst for the esterification of alcohol, and the results are shown in Table S5.† The reaction was performed at 60 °C using 1 bar of oxygen in the presence of K_2CO_3 . The oxidation of alcohols proceeds relatively completely, yielding esters with high selectivity in excellent yields (entries 1–8). Both electron-donating (–CH₃ and –OCH₃) and electron-withdrawing groups (–Cl) on the alcohols have little effect on the reaction yield or selectivity. In addition, the spatial group effect has little impact on the reaction. However, alcohols substituted with –NO₂ need a long time to obtain a high yield (entry 9). The results show that Co–N–C-800 has excellent properties, which can be used in many kinds of molecular transformation reactions.

3.3. DFT calculations

To understand the incorporation effect of Co, several possible configurations of Co–N_x–C_y models were considered and optimized as shown in Fig. S9.† For the aspect of relative energy, the substrates with plane quadrilateral coordination of Co atom (four-fold coordination) were always the more stable configurations. However, for catalytic reactions, catalyst surface with coordinatively unsaturated sites (CUS) possess high catalytic activity, and full coordination of the Co atom in the graphene plane may not improve the reactivity. As a result, we further calculated the adsorption energy of DMPS on different substrates. As shown in Fig. 5, energetically favoured configurations of typical Co–N_x–C_y (x = 2-4) structures are presented.

Besides, the other possible configurations of Co-N_x -C_y with different Co-N coordination are also considered and shown in Fig. S10.† Among these, the bulge of the Co atom in Co-N₂-C₁, Co-N₃-C, and Co-N₃-C₂ significantly increased the adsorption strength of DMPS, while for Co-N₂₊₂-C of Co-N₄, the Co atom



Fig. 5 The investigated stable structures of DMPS adsorption on Co– N_x – C_y (x = 2-4), as well as the adsorption energy and bond length of Si–H. The gray, blue, light blue, yellow and white balls represent carbon, nitrogen, cobalt, silicon, and hydrogen atoms, respectively.

was retained in the basal plane, and the adsorption energy was only ~1.71 eV. All the bond lengths of Si–H were increased, compared to the Si–H of DMPS in the gas phase (1.496 Å), suggesting the activation of the Si–H bond. In particular, for Co–N₃, the Co atom was bonded with both the H atom and Si atom, and it induced the longest Si–H bond, indicating the highest catalytic activity, which is coincident with the experimental observations mentioned above.

In order to understand the nature of the highest catalytic activity of Co-N₃-C, we also plotted the electron densities of the DMPS molecule, bare Co-N3-C substrate, and DMPS adsorbed on the Co-N₃-C surface as shown in Fig. 6. The electrical properties of the Co atom were positive on the Co-N₃-C surface in the first place, during the process of adsorption, charge transfer occurred between the Co atom and the DMPS molecule, by which the adsorption strength was augmented. Therefore, we can conclude that the coordinative unsaturation of the Co atom and the bulge of the Co atom above the Co-N3-C surface is beneficial for reducing the steric hindrance between the reactant and the basal plane. Furthermore, the charge transfer between dimethylphenyl-silane and the Co-N₃-C surface also augment the activation of the Si-H bond, which can be considered as the essential reason for the highest catalytic activity of Co-N₃.

Combined with the experimental results and the literature of the metal-catalysed oxidation of DMPS,⁴⁷ a possible mechanism is given in Fig. 7a. A representative Co–N₃–C structural model was used to evaluate the whole reaction cycle. The reac-



Fig. 6 The electron density of (a) DMPS, (b) Co–N₃–C substrate, and (c) adsorbed DMPS on Co–N₃–C. Isovalue = 0.5 a.u.



Fig. 7 (a) Proposed pathway for the hydrolysis of organosilanes catalysed by Co-N-C-800. (b) Oxidation of DMPS over Co-N₃-C. TS, transition state. The values denote the relative energy referenced to the initial state.

tion began with the insertion of the Si-H bond into the active Co centre to generate a silyl-metal hydride intermediate. The silyl-metal hydride intermediate was subsequently attacked by a nucleophile derived from water to generate the silanol and release hydrocarbon gases. Moreover, to reveal the catalytic activity of Co-N₃-C, the energy (the values denote the relative energy referenced to the initial state) of each step along the reaction cycle has been calculated (Fig. 7b). At the beginning of the reaction, a DMPS molecule dissociatively adsorbed on the graphene surface. The bulk molecule was bonded to the Co atom of one Co-N₃-C site through the Si atom and the H proton was captured by another Co-N₃-C site with an adsorption energy of -6.43 eV, which is even more than the adsorption energy of DMPS on a single Co-N₃-C site. Then, a water molecule approached the surface of Co-N₃-C through van der Waals force and attacked the Co-Si bond with an activation energy of +1.62 eV. Finally, the two H atoms bonded as a H₂ molecule with an activation energy of +1.39 eV. For a certain catalytic reaction, it is well known that the reaction could proceed at a relatively fast rate if the activation barrier is below 2.0 eV.48 Therefore, the oxidation of DMPS could be catalyzed over Co-N₃-C under moderate conditions because the activation barriers of each step were all around 1.5 eV, which reflects good catalytic performance of Co-N3-C. Besides, calculation of the energy of the reaction path could also provide a criterion to verify the validity of the oxidation cycle of DMPS.

4. Conclusion

In conclusion, we developed a facile approach to synthesize SAC Co–N–C catalysts *via* the one-step pyrolysis of the cobalt–phenanthroline complexes on porous MgO sheets after acid leaching. The structure of the as-synthesized Co–N–C catalysts has been characterized by HAADF-STEM, XPS, XAFS, and WT, and the coordination number of Co with N is reduced with an increasing pyrolysis temperature. The Co–N–C-800 catalyst exhibits good catalytic activity, great chemoselectivity, and good recyclability for the oxidation of organosilanes. The great catalytic performance comes from the charge transfer between DMPS and high Co–N₃ content, and many atomically dispersed Co active sites, which is proved by the control experiments and DFT calculations. Moreover, the Co–N–C-800 catalyst also shows

good catalytic activity for the oxidative esterification of alcohols. This work may provide a cheaper and more efficient catalyst for the oxidation of organosilane at a large scale.

Author contributions

Fan Yang, Zhihui Liu conceived and designed the experiments. Zhihui Liu and Andong Feng performed laboratory experiments. Bing Zhang and Wang Yang conducted part of the characterization analysis of the material. Xiaodong Liu provided theoretical calculation and discussion. Yongfeng Li and Fan Yang were responsible for planning and supervising the project.

Conflicts of interest

There are no conflicts to declare.

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