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Introduction

Indoor air quality is closely related to human health.¹ As one of the main pollutants in the indoor environment, formaldehyde, is a colorless and irritating gas, which is easy to volatilize at room temperature.^{2,3} Exposure to formaldehyde even as low as 0.3–0.5 ppm over a short period of time can cause irritation of the eyes and nasal passages.⁴ Exposure to formaldehyde at larger than 1 ppm concentration for an extended time causes serious health issues, such as lung function decline, liver injury, and other pathologies.⁵ Removing formaldehyde from indoor air is particularly vital to maintain human health since more than 80% of the time in people's lives is spent indoors.⁶

Catalytic oxidation is a promising technology to remove formaldehyde in indoor environments.^{7,8} Formaldehyde can be

Excellent room temperature catalytic activity for formaldehyde oxidation on a single-atom iron catalyst in a moist atmosphere†

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For human safety, efficient removal of formaldehyde in indoor environments is essential. However, removing formaldehyde from indoor environments given the low-temperature and moisture content remains a challenge. In this study, a metal–organic framework-based single-atom iron catalyst (Fe_{SA}) is proposed as a candidate catalyst for formaldehyde oxidation. The adsorption characteristic and the reaction path over Fe_{SA} with different coordination environments were explored using density functional theory (DFT) calculation. Guided by the theoretical results, Fe_{SA} with 5-nitrogen coordination (Fe_{SA}–N₅–C) was selected and prepared for activity testing. The activity tests revealed that the removal efficiency of formaldehyde reached 85.8% at 25 °C and 75% relative humidity, which is far higher than currently reported data. More importantly, moisture can boost catalytic oxidation of formaldehyde through reduction of the energy barrier and activation of the O₂ molecule, illustrating that Fe_{SA}–N₅–C is robust enough for practical applications. We propose a new catalyst design route for removing formaldehyde from indoor environments, aiming for high low-temperature activity, strong water-resistance, and long-term stability.

converted into carbon dioxide and water with the assistance of a catalyst. This method has significant advantages of requiring simple equipment, exhibiting no secondary pollution and having high efficiency. Traditional catalysts mainly include precious metal and metal oxides.9 Platinum (Pt),10,11 aurum (Au),^{12,13} and argentum (Ag)^{14,15} are currently used for catalytic oxidation of formaldehyde. Although precious metals can achieve 100% removal efficiency (RE) above 100 °C, catalytic activities at room temperature are less effective, such as only 12% RE for the gold/iron-oxide catalyst and less than 10% RE for Ag/ TiO₂.^{14,16} In addition, the high price of precious metals also limits their industrial application.9 Considering metal oxides, MnO₂/cellulose composites can completely degrade 100 ppm HCHO at 140 °C, but only achieve 15% RE at 60 °C.17 CoMnoxide catalysts can catalyze the oxidation of 80 ppm formaldehyde into CO₂ and H₂O at 60 °C, while only 23% of formaldehyde can be converted at 30 °C.18 Therefore, it is crucial to develop novel catalysts with high catalytic activity at room temperature.

In addition, the water resistance of catalysts is another important requirement for removing formaldehyde, due to the relative humidity (RH) of 50 to 70% in indoor environments.¹⁹ If the catalyst is not resistant to water, its activity suffers.^{20,21} According to Pei *et al.* the RE of formaldehyde on PtRu/ $Ce_{0.7}Zr_{0.3}O_2$ is 72% RE at 0% RH, while the RE is reduced by 7% with the introduction of 5 vol% water vapor.²² Similarly, the RE of formaldehyde on Fe₂O₃/TiO₂ drops by 31% at 50% RH.²³

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However, in an actual air environment, the humidity is obviously higher than under experimental conditions (5 vol% water vapor), indicating that the RE of formaldehyde on those catalysts may be inferior. Therefore, the ability to achieve efficient catalytic oxidation at room temperature with robust water resistance is key to the removal of formaldehyde.

Based on the above literature, there are two factors leading to the unsatisfactory removal ability of conventional catalysts in practical application environments: poor low-temperature activity and weak water resistance. Conventional catalysts are unable to activate oxygen molecules at low temperatures, leading to the high energy barrier of catalytic oxidation for formaldehyde and poor low-temperature activity. On the other hand, the poor selectivity of conventional catalysts results in the active sites of catalysts being occupied by water molecules preferentially. Therefore, a catalyst with high catalytic activity and high adsorption selectivity urgently needs to be developed.

Compared with conventional catalysts, single-atom catalysts (SACs) exhibit many superior properties, including high catalytic activity, high adsorption selectivity and high metal atom utilization.²⁴ SACs show excellent performance in fuel cells,²⁵ electrocatalytic reduction of CO2,26 and hydrogenolysis.27 In addition, SACs also have application potential in volatile organic compound incineration and degradation of toluene.28,29 Similarly, SACs exhibit excellent properties in the field of catalytic oxidation: Fe_{SA} shows high catalytic activity for the catalysis of benzene,³⁰ methane,³¹ and mercury³² at room temperature. Reactants have a lower energy barrier for catalytic oxidation or may create reaction-promoting free radicals on the surface of SACs, which is beyond the reach of conventional catalysts. In the study of catalytic oxidation of CO, single-atom Pt exhibited high selectivity for O2 and weak bonding for CO, which facilitated the reaction between O₂ and CO molecules.³³ Therefore, SACs with high activity and high adsorption selectivity are the targets of our study.

Based on the advantages of SACs, we propose an ironnitrogen doped carbon-based SAC for catalytic oxidation of formaldehyde. Carbon materials such as graphene are good catalyst carriers given their large specific surface areas and their ability to form strong interactions with metal atoms and high thermal conductivity.34,35 Moreover, single vacancy and double vacancies in carbon materials act as doping sites for active centers.36 Metal atoms can be anchored on the carbon lattice by bonding with nitrogen atoms inserted into vacancy defects of carbon materials to anchor iron atoms more firmly. At present, iron-nitrogen doped carbon-based SACs have been synthesized and their performance has been tested in the laboratory.37 Ironnitrogen doped carbon-based SACs as catalysts (FeN₃ and FeN₄) exhibited high catalytic activity towards the oxygen reduction reaction (ORR).^{38,39} However, there are few reports devoted to the removal of formaldehyde by SACs at room temperature.

In this study, we innovatively developed and optimized a novel double-layer structure of an iron–nitrogen doped carbon-based SAC (Fe_{SA}–N₅–C). Fe_{SA}–N₅–C was screened as the best catalyst based on the adsorption energy and reaction energy barriers among three catalysts (Fe_{SA}–N₃–C, Fe_{SA}–N₄–C and Fe_{SA}–N₅–C). Second, the differences among three catalysts are revealed by the

relationship between Δ_{L-H} (defined by the difference between the LUMO of gases and the HOMO of the single-atom iron catalyst) and adsorption energy. In terms of experiments, we synthesized samples of iron–nitrogen–carbon (Fe–N–C) catalysts using pyrolysis of metal–organic framework materials. Transmission electron microscopy (TEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) are used to analyze the morphology of Fe–N–C and the existing form of the Fe element on Fe–N–C. The coordination environment of Fe–N–C is also observed based on analyses including X-ray absorption near edge structure and extended X-ray absorption fine structure. Finally, we conducted activity evaluation experiments and found that Fe–N–C has an excellent removal efficiency of 85.8% at room temperature and 75% RH conditions, as well as water resistance of the catalyst.

Methods

Theoretical calculation methods

Density functional theory (DFT) simulations are conducted using the Vienna *ab initio* simulation package (VASP) software.⁴⁰ The core region electrons were approximated by the projector augmented-wave (PAW) method, where the kinetic energy cutoff of the plane wave base was set to 500 eV.⁴¹ The exchange correlation was calculated using generalized gradient approximation (GGA) functions. The effect of spin polarization was taken into account to avoid errors in the calculations due to the magnetic properties of the iron atoms. To obtain a more accurate interaction between the catalyst and gas molecules, van der Waals (VdW) interaction was considered by adopting the DFT-D₃ correction.⁴² A 4 × 4 graphitic carbon supercell was chosen as the substrate for the catalyst, while the vacuum layer height was set at 15 Å.

In the calculation of geometry structures, a 7 \times 7 \times 1 Γ centered k-point grid was used according to the convergence test results, and subsequent self-consistent calculations were carried out by using a $15 \times 15 \times 1$ Γ -centered k-point grid to obtain more accurate energy values.²³ The geometry calculation achieved convergence when the calculated energy difference drops below 1×10^{-5} eV and the force difference falls below 0.05 eV Å⁻¹.43 To obtain more accurate transition state configurations, the climbing image nudged elastic band method (CI-NEB) was first used to search for transition states and achieve fast convergence with a loose force convergence criterion (0.1 eV Å⁻¹).⁴⁴ In terms of geometric optimization calculations, the coarser transition state images were refined by the improved dimer method (IDM) to obtain more accurate transition state configurations, with the convergence criterion for refinement set at 0.05 eV Å⁻¹. In addition, the detailed setting of DFT calculation is described in the ESI.†

Gibbs free energies are calculated using vaspkit,⁴⁵ and the calculation is from:

$$G = E_{\rm ele} + E_{\rm ZPE} + E_{\rm H} - TS \tag{1}$$

where E_{ele} denotes the energy calculated by DFT at 298 K; E_{ZPE} denotes the zero-point energy deduced by frequency

calculation; $E_{\rm H}$ denotes the energy contributed by enthalpy; R denotes the gas constant; T denotes the reaction temperature; S denotes the entropy (gas entropy values are from the NIST database⁴⁶ and the surface entropy values are from vaspkit⁴⁵).

To consider the contribution of entropy, we adopt the Gibbs free energy to calculate the adsorption properties of gas molecules on the catalyst surface, and the adsorption energy of the gas (G_{ads}) is calculated according to:

$$G_{\rm ads} = G_{\rm tot} - G_{\rm gas} - G_{\rm sub} \tag{2}$$

where $G_{\rm tot}$ represents the total energy of the system after gas adsorption, $G_{\rm gas}$ represents the total energy of isolated gas molecules, and $G_{\rm sub}$ represents the energy of the graphenebased substrate. The more negative the value of $G_{\rm ads}$, the stronger the adsorption interaction. The temperature is set to 298 K for the adsorption energy calculation.

The variation of Gibbs free energy (ΔG) for the energy barrier ($\Delta G_{\rm b}$) and reaction heat ($\Delta G_{\rm h}$) are calculated respectively from:

$$\Delta G_{\rm b} = G_{\rm TS} - G_{\rm IS} \tag{3}$$

$$\Delta G_{\rm h} = G_{\rm IM} - G_{\rm IS} \tag{4}$$

where G_{TS} denotes the energy of the transition state, G_{IS} denotes the energy of the initial state, and G_{IM} denotes the energy of the intermediate state.

Catalyst synthesis

In this study, iron–nitrogen–carbon (Fe–N–C) catalyst samples were prepared by the method of pyrolysis of metal–organic framework materials.^{47–49} First, 2-methylimidazole, $Zn(NO_3)_2$ · $^{6}H_2O$, and $Fe(NO_3)_3$ · $^{9}H_2O$ were dissolved in methanol and ultrasonically dispersed, then the mixed solution was transferred to a reaction vessel and heated at 130 °C for 4 hours. The heated material was washed three times with DMF and twice with methanol and dried overnight at 80 °C under vacuum to obtain the precursor Fe-ZIF-8. Next, the precursor precipitate was dried and ground into a powder form. Finally, the powder was calcined at 850 °C in a flowing nitrogen atmosphere for 2 hours, then cooled to room temperature after calcination to obtain the catalyst sample.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Miniflex 600 X-ray diffractometer from Rigaku, Japan, using X-rays to characterize the powdered catalyst samples. The X-ray source for the test was generated by excitation of K α by a Cu target at a wavelength of 0.154 nm. Scanning electron microscopy (SEM) analysis was carried out on a GIMINER 300 microscope (Carl Zeiss, Germany) with an accelerating voltage of 3 kV. To analyze the specific surface area properties of Fe–N–C, its Brunauer– Emmett–Teller (BET) surface area test was carried out by using N₂ isothermal adsorption at 77 K. The samples were deposited on a silicon substrate and the surface was sprayed with gold before characterization. Transmission electron microscopy (TEM) characterization was performed on an FEI Talos F200x (Thermo Fisher Scientific, USA) with an acceleration voltage of 120 kV. Super-X spectroscopy was also done to evaluate the structure and geometry of the catalyst. The catalysts were dispersed by an ethanol ultrasonic wave and prepared on an ultra-thin copper grid. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was conducted on a Titan Themis 60-300 with 200 kV test voltage.

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To further verify the fine structure of the prepared catalyst is consistent with theoretical screening, it was analyzed by X-ray absorption fine structure spectroscopy (XAFS) at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (Beijing, China). Fe K-edge XAFS was acquired and the raw data were processed by using the Athena and Artemis modules in the IFEFFIT software packages.⁵⁰ The amplitude reduction factor (S_0^2) was fixed at 0.91. Fe K-edge theoretical XANES was simulated using the FDMNES code in the full multiple-scattering (FMS) mode.^{51,52} The energy-dependent Hedin–Lundqvist exchange–correlation potential was used in the calculation, and the cluster radius satisfied convergence requirement.

Catalytic activity experiment

A schematic diagram of the catalyst activity evaluation device is shown in Fig. 1a.

During the experiment, 50 mg of catalyst was carefully loaded into a quartz reactor with an inner diameter of 6 mm which was placed in a tube furnace (Fig. 1a®). The initial concentration of formaldehyde was 60 ppm with a total gas flow rate of 150 mL min⁻¹. A gas hourly space velocity (GHSV) of 73 000 h^{-1} was used in experiment. To test the catalytic efficiency of formaldehyde at different temperatures, the reaction temperature range was set from 25 to 170 °C, with temperature intervals of 20 °C. High-purity nitrogen and oxygen were adjusted to the total gas flow with the ratio of 79:21. A gas scrubber (Fig. 1a⁽¹⁾) filled with paraformaldehyde particles of a certain quality was heated in a water bath pot, and the volatilized paraformaldehyde vapor was carried by nitrogen into the pyrolysis furnace (Fig. 1a④) where paraformaldehyde steam was depolymerized into formaldehyde gas at a temperature of 160 °C. Subsequently, ormaldehyde gas was catalytically degraded in a tube furnace (Fig. 1a®). Moreover, the calculation of RE of the catalyst requires a formaldehyde calibration curve. The procedure for absorbance determination of formaldehyde standard solution with the calibration curve obtained after the determination is shown in Fig. 1b and S1,† respectively. In addition, the detailed processes of catalytic oxidation for formaldehyde are described in the ESI.[†]

The concentration of formaldehyde gas at the inlet and outlet of the reactor was measured according to the above operating procedure, and the RE of formaldehyde ($\eta_{\rm HCHO}$) was calculated from:

$$\eta_{\rm HCHO} = \frac{c_{\rm HCHO}^{\rm in} - c_{\rm HCHO}^{\rm out}}{c_{\rm HCHO}^{\rm in}} \times 100\%$$
(5)

where $c_{\text{HCHO}}^{\text{out}}$ represents the formaldehyde concentration at the reactor inlet and $c_{\text{HCHO}}^{\text{in}}$ is the formaldehyde concentration at



Fig. 1 (a) Schematic diagram of the catalyst activity evaluation device. (b) Procedure for absorbance determination of formaldehyde standard solutions used to calculate the concentration of formaldehyde solution in the absorber bottle of the active device.

the reactor outlet. To ensure adequate reaction time, each working condition was continuously operated for 40 minutes.

Results

Catalyst model and selective adsorption

Considering the effect of the coordination number on the adsorption characteristics and catalytic activity, we constructed three different single-atom iron catalysts, as shown in Fig. 2a. According to the number of coordinated nitrogen atoms, these three catalysts are named $Fe_{SA}-N_3-C$, $Fe_{SA}-N_4-C$ and $Fe_{SA}-N_5-C$, respectively. For $Fe_{SA}-N_5-C$, the interlayer nitrogen atoms are embedded in two layers of $Fe_{SA}-N_4-C$ and one nitrogen atom is shared by two iron atoms in the upper and lower layers. The main parameters of the three models, including the bond length (*d*), iron atom charge (q_{Fe}), prominence height (*h*), formation energy (E_{for}) and binding energy (E_{bin}), are listed in

Table 1. The main parameters of the three catalysts are similar to those of previous studies, ^{53–55} proving that our DFT calculation should be reasonable and credible. The $E_{\rm for}$ of the three catalysts are all below zero, indicating that these configurations are thermodynamically favorable and stable. Moreover, the binding energies of the three single-atom iron catalysts are all lower than the cohesion energy of Fe (-4.28 eV), ⁵⁶ suggesting that those catalysts can be firmly anchored by a nitrogen-doped substrate. Based on above analysis, these catalysts should be stable, which has also been proved by a previous study.⁵¹

Then, we investigate the adsorption characteristic of gases on the three catalysts. The geometric configurations, entropy and important information in the adsorption process of O₂, HCHO, CO₂, and H₂O are shown in Fig. 2b and Tables S2–S6.† Fe_{SA}–N₃–C can form stable bonds with all four molecules, while Fe_{SA}–N₅–C can form stable bonds only with the O₂ molecule. In addition, the Gibbs free adsorption energy (G_{ads}) of the four



Fig. 2 (a) Structural diagrams of $Fe_{SA}-N_3-C$, $Fe_{SA}-N_4-C$, and $Fe_{SA}-N_5-C$. (b) Adsorption state of reactants (O₂ and HCHO) and products (CO₂ and H₂O) on the catalyst surface. (c) Gibbs free energy for adsorption energy (G_{ads}) of the four gas molecules on the surface of the catalysts.

gases on the catalysts were calculated based on eqn (1) and (2), as shown in Fig. 2c. The $G_{\rm ads}$ values of the four gases on Fe_{SA}–N₃–C are obviously greater than those of the others, which is consistent with their adsorption configurations. In detail, the

value of G_{ads} for the four gases are all below -0.4 eV, indicating that the adsorption process is chemical adsorption. To facilitate the reaction cycle of HCHO oxidation and obtain strong water resistance, the adsorption of CO₂ and H₂O on the catalyst

Table 1 Bond length, relative height of the Fe atom, charge of Fe, formation energy and binding energy for the three single-atom iron catalysts

	d_1 (Fe–N)/Å	d_2 (C–N)/Å	$h/{ m \AA}$	$q_{ m Fe}/ m e$	$E_{\rm for}/{ m eV}$	$E_{\rm bin}/{\rm eV}$
Fe _{SA} -N ₃ -C Fe _{SA} -N ₄ -C Fe _{SA} -N ₅ -C	$\begin{array}{c} 1.78 \; (1.79)^{54} \\ 1.89 \; (1.92)^{55} \\ 1.92 \end{array}$	$\begin{array}{c} 1.37 \ (1.37)^{54} \\ 1.38 \ (1.36)^{55} \\ 1.36 \end{array}$	$\begin{array}{c} 1.25 \ (1.23)^{54} \\ 0 \ (0.04)^{55} \\ -0.32 \end{array}$	$\begin{array}{c} \textbf{0.89} \ (\textbf{0.90})^{54} \\ \textbf{1.07} \ (\textbf{1.08})^{55} \\ \textbf{1.04} \end{array}$	$\begin{array}{c} -0.80 \ (-0.81)^{53} \\ -3.27 \ (-3.25)^{53} \\ -8.63 \end{array}$	$-4.79 \left(-4.55\right)^{53} \\ -7.00 \left(-7.12\right)^{53} \\ -10.05$

surface should be weak. Compared with the adsorption energy of H₂O on CeO₂ (1 1 1) (-0.69 eV),⁵⁷ G_{ads} of H₂O on Fe_{SA}-N₅-C (-0.19 eV) is closer to zero, suggesting that Fe_{SA}-N₅-C should have stronger water resistance than CeO₂. Considering the water resistance and product desorption, Fe_{SA}-N₅-C should be a potential candidate for HCHO removal among the three catalysts. However, Fe_{SA}-N₃-C may have higher catalytic activity for HCHO oxidation due to its high O₂ adsorption energy. To further explore its catalytic activity, the reaction path and activity analysis were performed.

Reaction path and activity analysis

In this section, the transition state structures were located to explore the reaction path and the rate-determining step. The screening of catalytic activity was carried out among the three catalysts to determine the theoretical configuration of catalysts used for experimental preparation. The identified reaction paths for the three catalysts are plotted in Fig. 3.

For Fe_{SA}-N₃-C, the reaction path for catalytic oxidation of HCHO is shown in Fig. 3a. First, O₂ and HCHO molecules form a five-membered peroxide ring structure of O–O–C–O–Fe (IM1). In this process, the O–O bond is extended from 1.43 Å (TS1) to 1.50 Å (IM1), as shown in Fig. S2a.† Due to the instability of the peroxide ring, it breaks into adsorbed OH and HCOO (IM2). As the HCOO group rotates, the hydrogen atom moves from the HCCO group to the OH group and forms the H₂O molecule (IM4). Finally, CO₂ and H₂O molecules are desorbed from the catalyst surface (FS).

For Fe_{SA}–N₄–C, the reaction path for catalytic oxidation of HCHO is shown in Fig. 3b. Like Fe_{SA}–N₃–C, HCHO and O₂ molecules first form a five-membered peroxide ring structure of O–O–C–O–Fe with the Fe atom (IM6). In the process, the O–O bond is extended from 1.30 Å (IS2) to 1.41 Å (TS6) and eventually stretched to 1.44 Å (IM6), as shown in Fig. S2b.† Then, after the breakage of the five-membered ring, H atom combines with the lone O atom to form an intermediate structure with the OH group (IM7). Then the second dehydrogenation step takes place, while the H atom detaches from the HCOO group and produces H_2O and CO_2 molecules with the OH group (IM10). Finally, CO_2 and H_2O molecules are successively desorbed from the catalyst surface (FS).

For Fe_{SA}–N₅–C, the reaction path for catalytic oxidation of HCHO is shown in Fig. 3c. First, HCHO attacks the lone oxygen atom of the O₂ molecule adsorbed on the catalyst (IM12). In this process, the O–O bond of the O₂ molecule is stretched from 1.30 Å (IS3) to 1.40 Å (TS12) and the interaction between the O atoms is weakened, as shown in Fig. S2c.† With the breaking of the O–O bond, one H atom detaches from HCHO and combines with

the O atom to form the OH group (IM13). Then, the structure of IM13 undergoes an adjustment, with OH and HCOO groups in favorable positions for the second dehydrogenation step. Immediately, the second dehydrogenation step takes place where the H atom detaches from the HCOO group and combines with the OH group to produce CO_2 and H_2O molecules (IM14). Finally, the catalytic cycle of HCHO oxidation on $Fe_{SA}-N_5-C$ is completed with the desorption of CO_2 and H_2O molecules from the catalyst surface.

Correspondingly, the variation of Gibbs free energy (ΔG) in the reaction path for the three catalysts is plotted in Fig. 3d, and the entropy of each state is summarized in Tables S7-S9.† For Fe_{SA}-N₃-C, the rate-determining step of catalytic oxidation is the process from IM3 to IM4, with an energy barrier of 1.26 eV. Subsequently, the products CO2 and H2O desorb from FeSA-N3-C with energy barrier of 0.33 and 0.76 eV, respectively. For Fe_{SA}-N₄-C, the rate-determining step of catalytic oxidation is the process from IS2 to IM6, with an energy barrier of 0.87 eV. The desorption energies of CO2 and H2O from the FeSA-N4-C surface are 0.19 and 0.39 eV, respectively. For Fe_{SA}-N₅-C, the ratedetermining step of catalytic oxidation is the process from IS12 to IM13, with an energy barrier of 0.67 eV. CO₂ and H₂O desorb from Fe_{SA}-N₅-C with 0.14 and 0.13 eV, respectively. Due to the weak adsorption interactions between the products (CO₂ and H₂O) and the catalyst surface, the desorption processes of the products are easy to take place, which is beneficial for the catalytic reaction cycle of HCHO oxidation. Satisfyingly, Fe_{SA}-N5-C has the lowest energy barrier for catalytic oxidation of HCHO, indicating that it has the highest catalytic activity among these three catalysts. Therefore, based on the above catalytic activity and water resistance, Fe_{SA}-N₅-C is a highly desirable candidate for later experimental preparation.

Catalyst characterization

Based on the route of high-temperature pyrolysis, the Fe–N–C sample was synthesized. To explore the structure and morphology of the catalysts, a series of characterization analyses were conducted on Fe–N–C, as shown in Fig. 4. The XRD pattern of the catalyst (Fig. 4a) reflects the crystallinity and phase structure of the Fe–N–C catalyst. The peaks at $2\theta = 22.7^{\circ}$ and 43.6° in Fe–N–C corresponding to the (002) and (101) of graphitic carbon, respectively. There is no obvious peak of the Fe compounds, indicating the absence of Fe particles in the synthesized Fe–N–C catalyst samples. The morphology of the Fe–N–C catalyst sample was observed through SEM images at 200 nm (Fig. 4b) and 100 nm resolutions (Fig. 4c). After the introduction of iron and high temperature pyrolysis, the morphology of Fe–N–C is also similar to that of ZIF-8, indicating



Intransic Reaction Coordinate

Fig. 3 Optimal pathway for the catalytic oxidation of formaldehyde on the (a) $Fe_{SA}-N_3-C$ surface, (b) $Fe_{SA}-N_4-C$ surface, and (c) $Fe_{SA}-N_5-C$ surface. (d) The energy changes of Gibbs free energy (ΔG) in the catalytic oxidation of formaldehyde on the three catalyst surfaces.

that the Fe–N–C sample can still maintain the pore structure. The N_2 isothermal adsorption curve of Fe–N–C is shown in Fig. 4d, and the BET specific surface area is 1219 m² g⁻¹, which

is similar to that of previous studies.^{58,59} The large specific surface area increases the contact probability between the reaction gas and the catalyst surface. Moreover, the TEM images



Fig. 4 XRD image (a), SEM images at 200 nm resolution (b) and 100 nm resolution (c), adsorption isotherm of nitrogen on the Fe–N–C surface at 77 K (d), TEM images at 100 nm resolution (e) and 50 nm resolution (f), HAADF-STEM image (g) and enlarged image (h) of the Fe single atoms derived from the Fe–N–C structure.

of the Fe–N–C catalyst taken at 50 and 20 nm resolutions are shown in Fig. 4e–f, respectively. The regular hexagonal structure of ZIF-8 is also observed in Fe–N–C and no Fe nanoparticles are found in the TEM images. The high angle annular dark field scanning transmission (HAADF-STEM) images of Fe–N–C (Fig. 4g–h) provide intuitive evidence that the Fe element is well uniformly distributed in the Fe–N–C sample, as shown in red circles.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were performed to determine the chemical state and coordination environment of iron sites inside Fe–N–C. XANES of Fe–N–C at the Fe K edge revealed a valence between Fe⁰(Fe foil) and Fe³⁺ (Fe₂O₃) that was slightly higher than that in iron phthalocyanine (FePc), as shown in Fig. 5a. Besides, there was a single major peak at 1.43 Å in the Fourier-transform (FT) EXAFS spectrum (Fig. 5b), which was similar to the Fe–N peak in the iron phthalocyanine reference, which revealed the character of the single atomic site. Further, to confirm the species of the coordination atoms and discriminate the backscattering atoms, wavelet transform (WT) analysis of EXAFS spectra was carried out (Fig. 5c). In Fe and FePc, WT maximum values were identified at 7.5 Å⁻¹ and 4 Å⁻¹, which represent the coordination shell of Fe–Fe and Fe–N, respectively. The contour intensity maximum of Fe–N–C well matched the location of Fe–N/O scattering and was similar to that of standard FePc. These results demonstrated that the structure of the metal atoms inside Fe–N–C is monodisperse. The EXAFS curve-fitting analysis showed clearly that the major peak at 1.43 Å was due to Fe–N and Fe–O shell coordination (Fig. 5d). The coordination



Fig. 5 XAFS characterization of Fe–N–C. (a) Fe K-edge XANES spectra. (b) and (c) Fourier-transformed and wavelet transform k^2 -weighted EXAFS signals. (d) Fitting results of the EXAFS spectrum in R space. (e) Comparison between the experimental spectrum of Fe–N–C and theoretical spectra.

numbers of the N and O atoms were estimated to be 5.1 and 1.0 at distances of 2.00 and 1.83 Å, respectively (Table S11†). XANES simulations (Fig. 5e) revealed the coordination characteristics of Fe–N–C, with Fe-atoms coordinated to five nitrogen atoms, which are in line with our expectations. Satisfactorily, Fe–N–C as prepared experimentally and Fe_{SA}–N₅–C as calculated theoretically are consistent.

Catalytic activity experimental verification

Considering that removing formaldehyde at room temperature is our desired goal, the RE of formaldehyde at 25 °C was first tested through eqn (5), as shown in Fig. 6a. To ensure that the RE of formaldehyde originates from catalytic oxidation rather than gas adsorption, we detected the tail gas through gas chromatography, as shown in Fig. S4.† There is an obvious peak of CO₂ accounting for 0.73% of the tail gas, which is 18 times more than that of indoor air (Table S12[†]).⁶⁰ Therefore, catalytic oxidation of formaldehyde over the Fe-N-C sample is the dominant factor for RE of formaldehyde. The RE of formaldehyde at 25 °C is about 85% (0% RH), which is significantly higher than the previously reported value,11,12,16,61-68 indicating that the Fe-N-C sample synthesized in the experiment has high catalytic activity at room temperature. In detail, the experimental conditions and RE of formaldehyde in the previous literature are listed in Table S13.† Compared with FeCo alloy@N-doped carbon (72.7% RE),61 the Fe-N-C sample has higher RE of formaldehyde, indicating that atomically dispersed Fe in Fe-N-C has higher catalytic activity than the FeCo alloy nanoparticles. In addition, there is no catalytic effect of nitrogen-doped carbon on formaldehyde removal due to its

zero the removel efficiency after 60 min (Fig. S5†). Therefore, we can exclude the influence of nitrogen-doped carbon on formaldehyde removal and confirm that the high catalytic activity of the Fe–N–C sample is thanks to the coordination unsaturated atomic iron.

Given that the moisture in air usually inhibits RE of formaldehyde, we compared the RE of formaldehyde over the Fe–N– C sample at 0% RH and 75% RH, as shown in Fig. 6b. Obviously, there is no inhibition effect of H_2O on formaldehyde removal, suggesting that Fe–N–C can work effectively in the actual working environment due to its strong water resistance. This strong water resistance of Fe–N–C can be well understood from its weak adsorption interaction with H_2O . To further testify the stability of the Fe–N–C sample, we performed the long-time activity testing in 8 hours under two experimental conditions (25 °C at 0% RH and 110 °C at 75% RH) as shown in Fig. S6–S7.† The RE of formaldehyde over the Fe–N–C sample under both testing conditions can be well maintained without any decay, suggesting that the stability of the Fe–N–C sample is robust.

When the temperature is below 110 °C, the RE of formaldehyde is similar under different RHs. However, there is a remarkable promotion effect of moisture on formaldehyde removal when the temperature is above 110 °C. Whether at 0% RH or 75% RH, the RE of formaldehyde increases with the increase of temperature, indicating that the temperature can accelerate the catalytic oxidation of formaldehyde. Significantly, the promotion effect of moisture on formaldehyde removal is more effective at higher temperatures. To further explore the promotion effect of moisture on formaldehyde removal, we compared the energy barriers of the rate-determining step with and without H_2O , as shown in Fig. 6c. Obviously, the energy



Fig. 6 (a) Comparison of Fe–N–C with other catalysts for RE of formaldehyde at 25 °C. (b) Column plot of formaldehyde RE at 0% RH and 75% RH at different temperatures with experimental error bars. (c) The effect of H_2O molecules for the energy barrier of the reaction rate-determining step on Fe_{SA}–N₅–C.

barrier of the rate-determining step reduces from 0.63 eV to 0.56 eV with the assistance of H₂O, suggesting that the promotion effect originates from facilitating the transfer process of the H atom from HCHO to the adsorbed O atom. In addition, the O–O bond length is slightly elongated from 1.29 Å to 1.30 Å in the presence of H₂O (Fig. S8†), indicating that moisture may promote formaldehyde removal through boosting the activation of the O₂ molecule. Therefore, the promotion effect of moisture

on formaldehyde removal can be well understood from the reduction of the energy barrier and activation of the O_2 molecule by moisture over Fe–N–C.

Catalytic activity analysis

To further understand the difference between the catalysts, we analyzed the relationship between oxygen adsorption energy and Gibbs free energy of the reaction, as shown in Fig. 7a.



Fig. 7 The linear relationship between ΔG and $E_{ads}(O_2)$ (a), the HOMOs of Fe_{SA}-N₃-C, Fe_{SA}-N₄-C and Fe_{SA}-N₅-C as well as the LUMOs of O_2 and HCHO (b), and the linear relationship between adsorption energies of gases (formaldehyde and oxygen) and corresponding Δ_{L-H} (c and d).

Obviously, there is a linear relationship between the adsorption energy of oxygen and the energy barrier, indicating that the lower adsorption energy of O₂ corresponds to the lower energy barrier of the reaction. To further deepen the understanding of relationship between adsorption energy and the electronic structure, we calculated the HOMOs and LUMOs of single-atom iron catalysts and gases (O2 and HCHO), as shown in Table S14.† During the gas adsorption, the electrons are transferred from the single-atom iron catalyst to O2 and HCHO (Tables S2-S4[†]). Based on the frontier orbital theory and the electron transfer in the adsorption process, we illustrated the HOMOs of Fe-N₃-C, Fe-N₄-C and Fe-N₅-C as well as the LUMOs of O₂ and HCHO, as shown in Fig. 7b. For convenience of expression, we define the difference between the LUMO of gases and the HOMO of the corresponding single-atom iron catalyst as Δ_{L-H} . The detailed value of Δ_{L-H} is highlighted by a dotted line with the corresponding color. Furthermore, we plotted the linear relationship between adsorption energy (E_{ads}) and Δ_{L-H} , as shown in Fig. 7c and d. Significantly, there is a linear relationship between Δ_{L-H} and adsorption energy, with the square of the correlation coefficient (R^2) above 0.96. In detail, the smaller the Δ_{L-H} , the stronger the corresponding adsorption energy, which is highly consistent with the frontier molecular orbital theory.⁶⁹ The space structure of the frontier orbital of the gas and the catalyst is shown in Fig. S9.[†] Obviously, the spatial structures of the HOMO for Fe_{SA}-N₃-C, are different from those of Fe_{SA}-N₄-C and Fe_{SA}-N₅-C. In detail, the HOMOs for Fe_{SA}-N₃-C match well with the LUMOs of O₂, which is consistent with the side-on adsorption configuration (Fig. 2b). In contrast, the endon adsorption configuration allows the formation of one bond between the LUMOs of O2 and the HOMO of FeSA-N4-C, as shown in Fig. 2b. In addition, the relationship between the dband center and adsorption energy was also explored, as shown in Fig. S10.† The closer the d-band center to zero, the greater the corresponding adsorption energy (Fig. S10b and c[†]). However, the square of the correlation coefficient based on the d-band center is obviously lower than that of Δ_{L-H} , indicating that the orbital matching principle in the frontier orbital theory is more suitable than the d-band center for this system. We hope this fundamental relationship between adsorption energy and the electronic structure can provide theoretical guidance for the design and optimization of novel catalysts for formaldehyde removal.

Conclusions

Aiming to design a robust catalyst for catalytic oxidation of formaldehyde indoors, DFT calculation is first performed to find the optimal coordination environment of Fe_{SA} based on the energy barrier and adsorption energy. Guided by DFT calculation, Fe_{SA} with 5-nitrogen coordination (Fe_{SA} -N₅-C) was successfully synthesized verified by X-ray absorption near-edge

structure and extended X-ray absorption fine structure analyses. The experimental results demonstrate that Fe_{SA}-N₅-C has an excellent removal efficiency of 85.8% at room temperature and under 75% RH conditions due to its lower energy barrier and prior adsorption of reactants based on DFT calculation. More important, the catalytic activity difference between SACs with different coordination environments of activity sites is revealed by oxygen adsorption and Δ_{L-H} . Surprisingly, the promotion effect of moisture on catalytic oxidation of formaldehyde originates from the reduction of the energy barrier and activation of the O₂ molecule by moisture over Fe-N-C. Therefore, the Fe_{SA}-N₅-C material is a promising catalyst to solve the problem of indoor purification of formaldehyde.

Conflicts of interest

There are no conflicts to declare.

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