Supporting Information

Excellent Room Temperature Catalytic Activity for Formaldehyde Oxidation on a Single-Atom Iron Catalyst in a Moist Atmosphere

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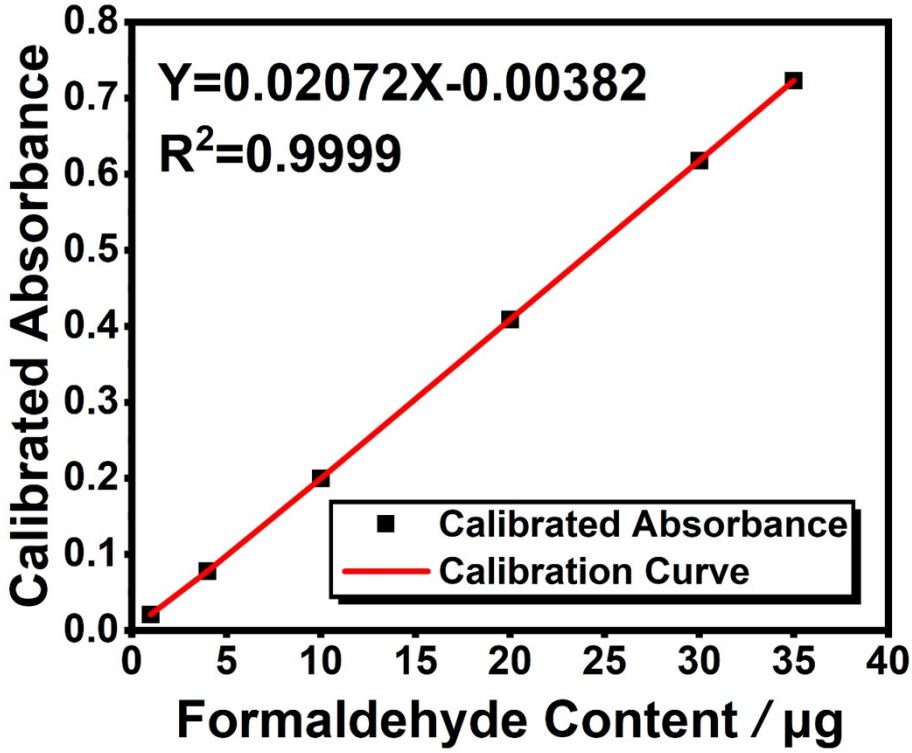

Fig. S1 Formaldehyde calibration curve.

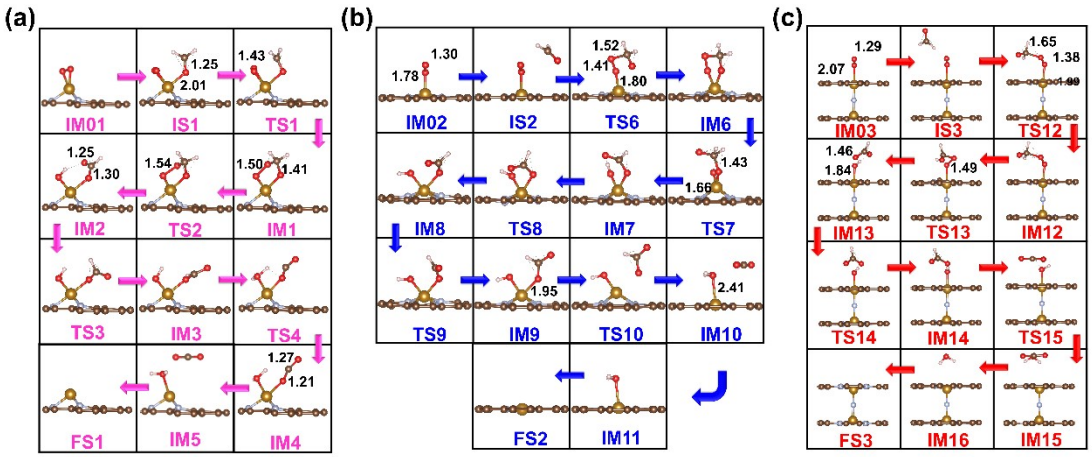

Fig. S2 Intermediate states, transition states, and bond length changes in the oxidation of formaldehyde on three catalyst surfaces.

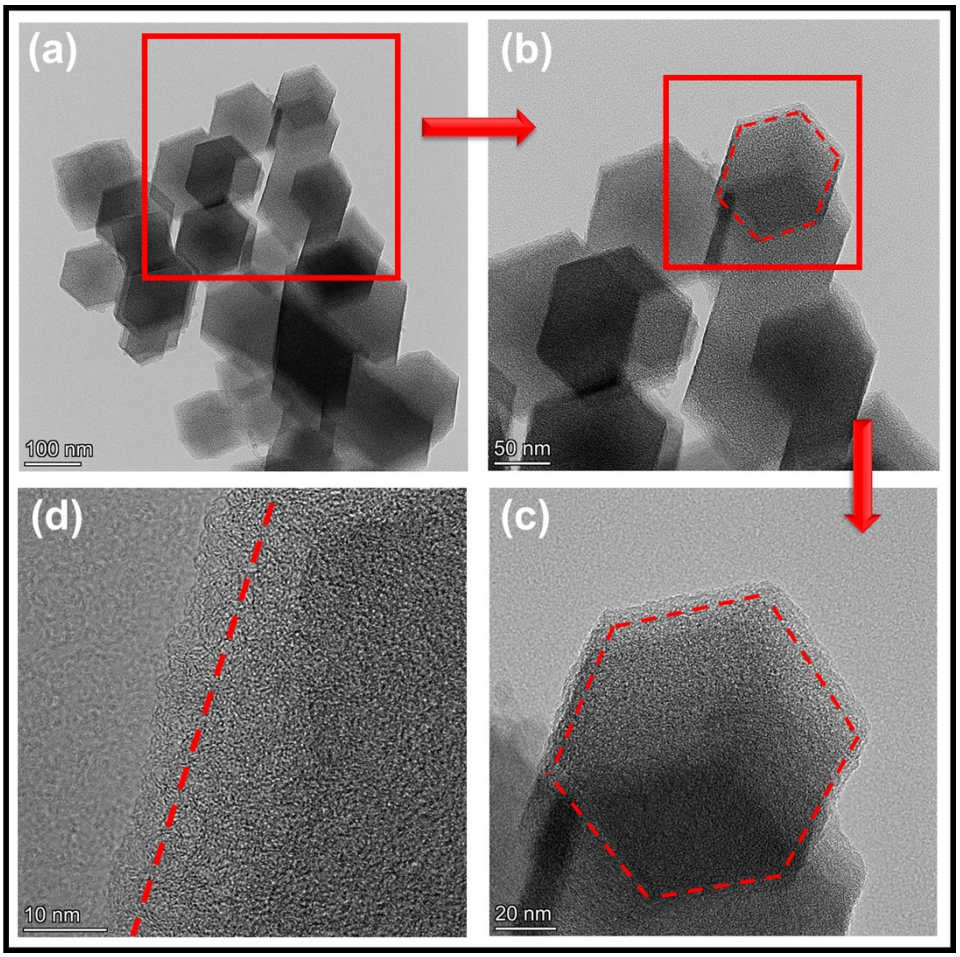

Fig. S3 TEM images of Fe-N-C sample at 10, 20, 50, and 100 nm.

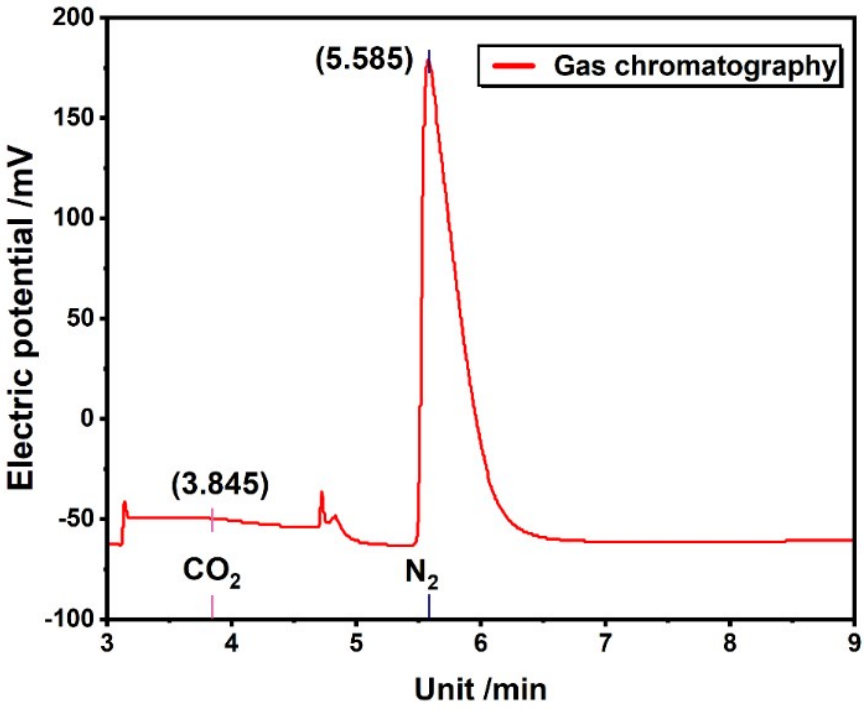

Fig. S4 Gas chromatogram of gas after fixed bed catalytic reaction.

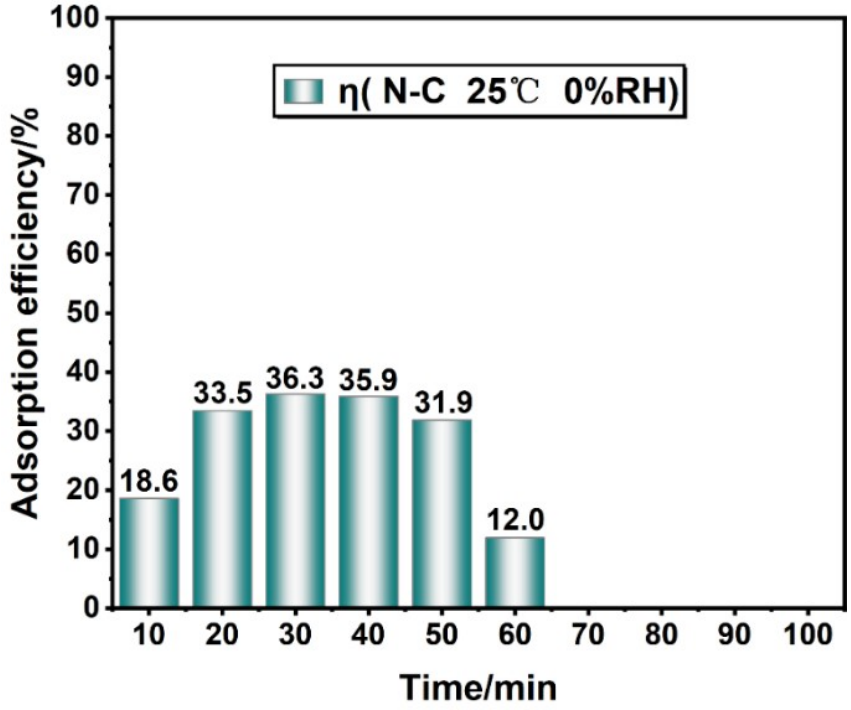

Fig. S5 Removal efficiency test of formaldehyde on nitrogen doped carbon materials at 25 ℃ and 0% RH.

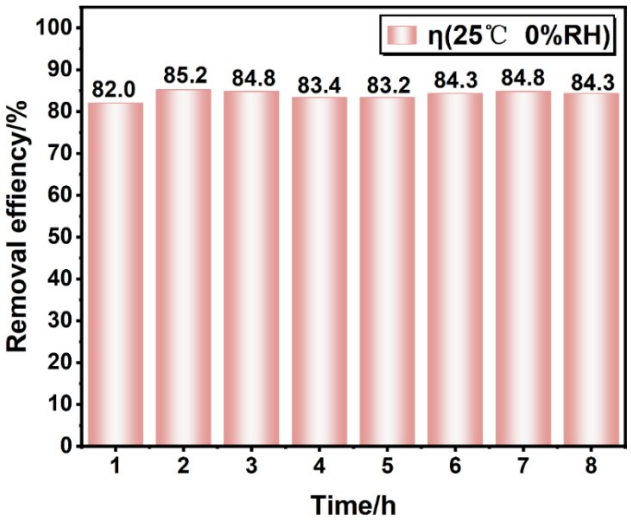

Fig. S6 Stability test results of Fe-N-C catalyst at 25 °C and 0% RH.

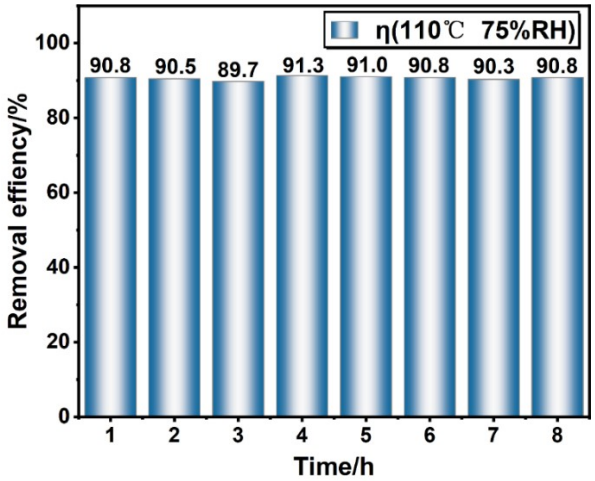

Fig. S7 Stability test results of Fe-N-C catalyst at 110 °C and 75% RH.

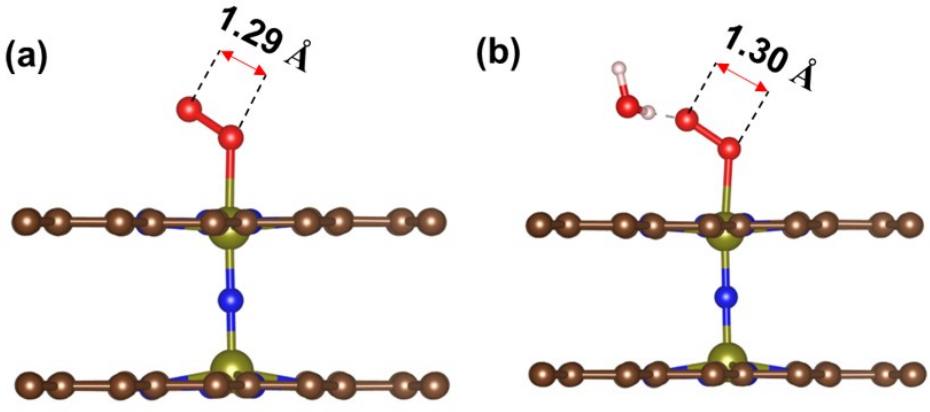

Fig. S8 Adsorptive configurations of O_2 on Fe_{SA}-N_5-C without H_2O (a) and with H_2O (b).

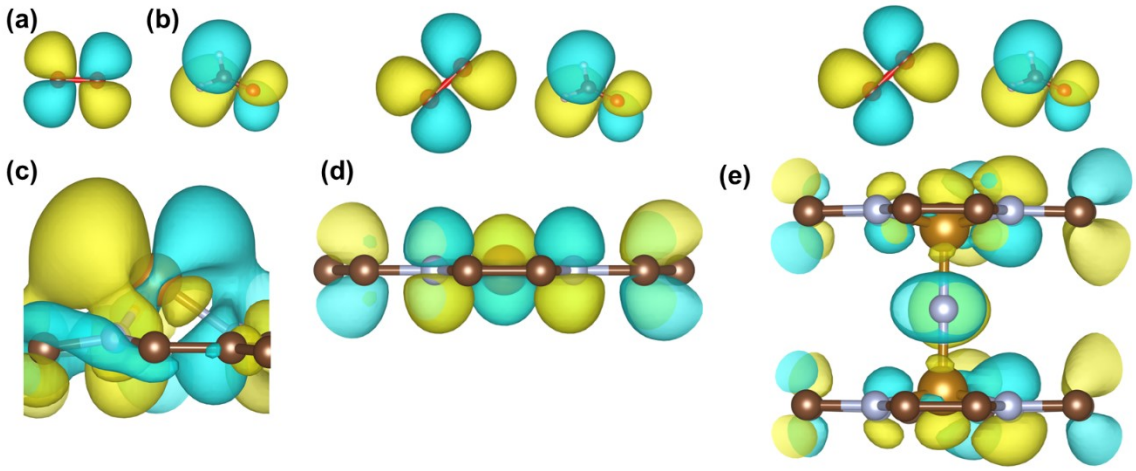

Fig. S9 The LUMO orbital distributions of oxygen (a) and formaldehyde (b); the HOMO orbital distributions of Fe_{SA}-N_3-C (c), Fe_{SA}-N_4-C (d) and Fe_{SA}-N_5-C (e).

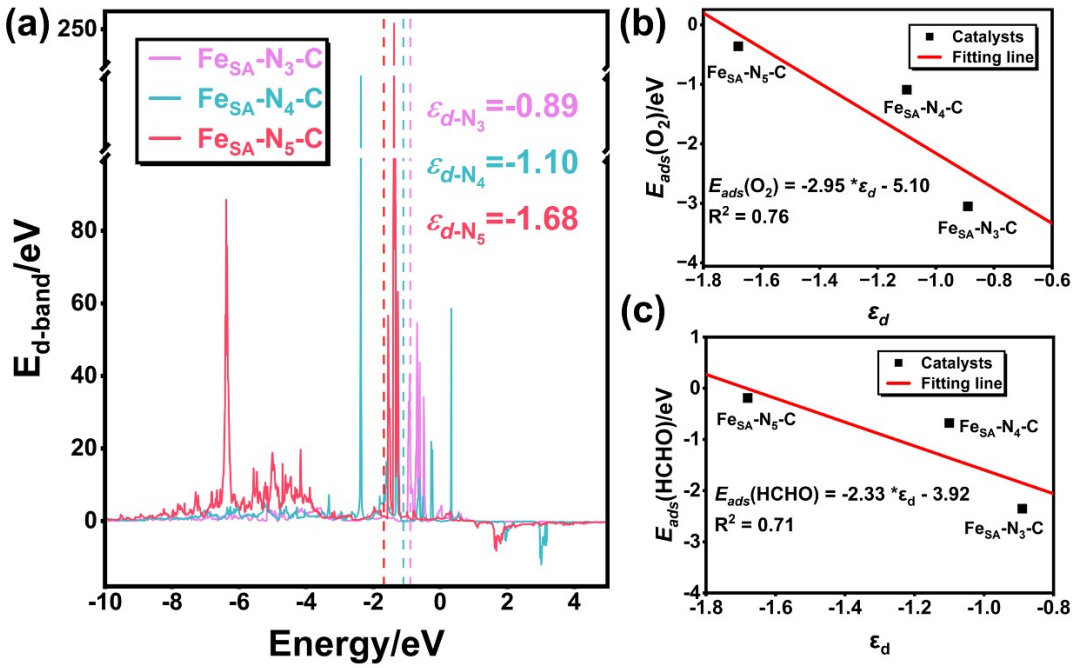

Fig. S10 The *d*-band centers (ε_d) of three catalysts (a), the relationship curve between $E_{ads}(O_2)$ and ε_d (b), with the relationship between E_{ads}(HCHO) and ε_d (c).

DFT Calculation:

To perform a thermodynamic analysis of the pathway to be selected, the heat of reaction at different reaction temperatures is calculated to express Gibbs free energy (ΔG_F) from:

$$\Delta G_F = G_{FS} - G_{IS} \quad \text{(S1)}$$

where G_{FS} (J·mol^{-1}) denotes the Gibbs free energy of the final state; G_{IS} (J·mol^{-1}) denotes the Gibbs free energy of the initial state.[1]

To analyze the structural stability of the catalyst, the formation energy (E_{for}) and the binding energy (E_{bin}) of the gas are calculated according to the following equations:

$$E_{for} = E_{tot} + x\mu_C - E_G - y\mu_N - E_{Fe} \quad \text{(S2)}$$

$$E_{bin} = E_{tot} - E_{sub} - E_{Fe} \quad \text{(S3)}$$

where E_{tot} is the total energy of the system; E_{sub} is the total energy of the graphene-based substrate; x is the number of carbon atoms removed from the pristine graphene; μ_C is the chemical potential of carbon defined as the total energy per carbon atom for pristine graphene; y is the number of nitrogen atoms added; μ_N is the chemical potential of nitrogen (defined as half of the total energy of an N_2 molecule); E_{Fe} is the total energy of an isolated Fe atom in the vacuum.[2]

The adsorption energy (E_{ads}) of gas without entropy is calculated according to the following equation:

$$E_{ads} = E_{tot} - E_{gas} - E_{sub} \quad \text{(S4)}$$

where E_{tot} is the total energy of the system; E_{gas} represents the total energy of isolated gas molecules; E_{sub} is the total energy of the graphene-based substrate.

The kinetic analysis of each reaction step is performed using conventional transition state theory, and the reaction equilibrium constant (k^{TST}) is calculated from:

$$k^{TST} = \frac{k_B T}{h} \times exp\left(\frac{-\Delta G_b}{k_B T}\right) \quad \text{(S5)}$$

where k_B (1.381×10^{-23} J·K^{-1}) is Boltzmann's constant; h (6.626×10^{-34} J·s) is Planck's constant; T (K) denotes the reaction temperature; ΔG_b (eV) denotes the reaction energy barrier expressed in Gibbs free energy expressed as the reaction energy barrier.[3]

Formaldehyde Removal Experiment:

To calculate the formaldehyde conversion rate of the catalyst, it is necessary to draw the formaldehyde calibration curve in advance. The procedure of absorbance determination of formaldehyde standard solution is shown in **Figure 1b**. First, filled the absorption tube with 20 mL of distilled water and collected 1 liter of the gas to be tested, and diluted the absorption solution to 50 mL. Accurately measured 5 mL of absorption solution in a 25 mL colorimetric tube and diluted to 10 mL, and then added 2 mL of 0.25% acetylacetone solution prepared in advance. Put the colorimetric tube into a water bath and heated it with boiling water for three minutes, then took it out and cool it to room temperature. Next, used a spectrophotometer to measure the absorbance value of the absorbing liquid. The model of the spectrophotometer is TU-1900, and the wavelength of the light source is 413 nm. Finally, subtracted the absorbance value of each standard solution and the absorbance value of the blank group (distilled water) to obtain a series of calibrated absorbance values, as shown in **Table S1**.

Table S1 Formaldehyde content of formaldehyde standard solution and calibrated absorbance value.

Tube no.	1	2	3	4	5	6
Formaldehyde content/μg	1	4	10	20	30	35
Calibrated absorbance	0.021	0.078	0.200	0.409	0.618	0.723

The calibration curve was plotted using the formaldehyde content as the horizontal coordinate and the calibration absorbance as the vertical coordinate, as shown in **Figure S1**. The equation for fitting the formaldehyde calibration curve is shown in **Equation S6**:

$$y = 0.02072x - 0.00382 \quad \text{(S6)}$$

In the formula, y represents the calibrated absorbance; x represents the formaldehyde content (μg).

Table S2 Vertical height difference, charge change of Fe atoms before and after molecular adsorption (Fe_{SA}-N_3-C).

Gas	Δh/Å	Δq_{Fe}/e	Δq_{sub}/e	Δq_{gas}/e
O_2	0.20	-0.33	-0.43	0.78
HCHO	0.36	-0.86	-2.82	3.7
CO_2	0.30	-0.87	-4.24	5.12
H_2O	0.33	-0.21	0.26	-0.07

Table S3 Vertical height difference, charge change of Fe atoms before and after molecular adsorption (Fe_{SA}-N_4-C).

Gas	Δh/Å	Δq_{Fe}/e	Δq_{sub}/e	Δq_{gas}/e
O_2	0.34	-0.12	-0.32	0.44
HCHO	0.43	-0.02	-0.36	0.38
CO_2	0.05	-0.02	-0.02	0.04
H_2O	0.15	-0.06	0.08	-0.02

Table S4 Vertical height difference, charge change of Fe atoms before and after molecular adsorption (Fe_{SA}-N_5-C).

Gas	Δh/Å	Δq_{Fe}/e	Δq_{sub}/e	Δq_{gas}/e
O_2	0.17	-0.14	-0.29	0.43
HCHO	-0.02	-0.04	0.06	-0.02
CO_2	-0.02	-0.02	0.05	-0.03
H_2O	-0.01	-0.02	0.04	-0.03

Table S5 Entropy of four gases at 298K and 1bar (calculated by NIST database).

S(eV/K)	O_2	HCHO	CO_2	H_2O
	0.00213	0.00229	0.00221	0.00197

Table S6 Entropy of four gases adsorbed on the surface of single atom catalyst (calculated by vaspkit).

S(eV/K)	O_2	HCHO	CO_2	H_2O
Fe_{SA}-N_3-C	0.00176	0.00211	0.00224	0.00188
Fe_{SA}-N_4-C	0.00204	0.00185	0.00215	0.0017
Fe_{SA}-N_5-C	0.00138	0.0016	0.00188	0.002

Table S7 Entropy of state in formaldehyde oxidation reaction on Fe_{SA}-N_3-C (calculated by vaspkit).

Fe_{SA}-N_3-C	IS	IM01	IS1	TS1
S(eV/K)	0.0024	0.00253	0.00269	0.00238
IM1	TS2	IM2	TS3	IM3

0.00213	0.00242	0.00214	0.00238	0.0025
TS4	IM4	IM5	FS	
0.00262	0.00341	0.00261	0.00342	

Table S8 Entropy of state in formaldehyde oxidation reaction on Fe_{SA}-N_4-C (calculated by vaspkit).

Fe_{SA}-N_4-C	IS	IM02	IS2	TS6	IM6
S(eV/K)	0.0024	0.00253	0.00269	0.00238	0.00213
TS7	IM7	TS8	IM8	TS7	TS9
0.00242	0.00214	0.00238	0.0025	0.00242	0.00211
IM9	TS10	IM10	IM11	FS	
0.00293	0.00274	0.00325	0.00353	0.00289	

Table S9 Entropy of state in formaldehyde oxidation reaction on Fe_{SA}-N_5-C (calculated by vaspkit).

Fe_{SA}-N_5-C	IS	IM03	IS3	TS12
S(eV/K)	0.0034	0.00339	0.00329	0.00208
IM12	TS13	IM13	TS14	IM14
0.00273	0.00216	0.00271	0.00263	0.00256
TS15	IM15	IM16	FS	
0.00268	0.004	0.00398	0.00331	

Table S10 Measurement of Fe content in catalyst.

Sample quality /mg	Constant volume /ml	**Measured element**	Meter reading	Unit	Converted content	Unit	**Mass fraction /%**
39.7	100	**Fe**	2.03	mg/L	5110.83	mg/kg	**0.51**

Table S11 Fe K-edge EXAFS curve fitting parameters for Fe-N-C.

Path	*CN*	*R* (Å)	σ^2 (Å^2)	ΔE_0	R_f, %
Fe-N	5.1	2.00	0.007	-4.2	1.7
Fe-O	1.0	1.83	0.002		

R represents the distance between absorber and backscatter atoms; *N* represents the coordination number; σ^2 represents the Debye-Waller factor to account for both thermal and structural disorders; ΔE_0 represents the inner potential correction; R-factor (R_f, %) indicates the goodness of the fit. The fitting range is 3.0 - 10.8 Å^{-1} in k space and 1.0 - 2.2 Å in R space.

Table S12 Contents of CO_2, N_2 and other gases in the tail gas.

CO_2 content	**N_2 content**	**Other gas content**
0.73%	92.42%	6.85%

Table S13 Performance of different catalysts for the oxidation of formaldehyde.

Catalyst	Reaction conditions			Conversion rate (%)	Refs.
	Concentration (ppm)	Airspeed (h^{-1}/L·h^{-1}·g^{-1})	Temp. (℃)		
FeCo@NC	100	-/60	25	72.7	4
Pt/H-Beta-TEA-12	400	-/60	25	62.8	5
$Ir_{0.75}Pt_{0.25}/Nb_2O_5$	240	-/60	25	60	6
0.5IrAl-CD	180	-/30	25	57.8	7
0.2wt% Pr/γ-Al_2O_3	30	-/24	25	47.2	8
0.2Pd@TS-1(30)	100	-/100	25	45	9
Ir/Nb_2O_5	240	-/60	25	37.2	6
Pt/Fe_2O_3	90	-/120	25	35.9	10
2wt% Au/CeO_2-Co_3O_4	8	-/15	25	30	11
1wt% Rh/TiO_2	100	50000/-	25	22.3	12
0.48wt% Au/Co_3O_4	8	-/15	25	22	11
2.52wt% Au/Fe-O	6.25	-/54	25	12	13
0.4wt% $Pt/ATiO_2$	50	-/30	25	11.2	14
Fe-N-C	**60**	**73000/180**	**25**	**85**	**This work**

Table S14 HOMO and LUMO orbitals of Fe-N_3-C, Fe-N_4-C, Fe-N_5-C, O_2 and HCHO.

	Fe-N_3-C	**Fe-N_4-C**	**Fe-N_5-C**	**O_2**	**HCHO**
HOMO (eV)	-1.79	-1.26	-0.91	-8.00	-6.18
LUMO (eV)	-0.86	-0.89	-0.57	-1.96	-2.70

Reference

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