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# **Electronic supplementary information (ESI)**

# Isopropanol as hydrogen source for single atom cobalt-catalyzed Wacker-type oxidation

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#### **General methods**

#### **Preparation of Catalysts**

The single atom dispersed Co–N/C catalyst was prepared according to the literature with an alteration of the support.<sup>1-3</sup> Briefly, a mixture of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.5 mmol, 124 mg) and 1,10-phenanthroline monohydrate (1.0 mmol, 198 mg) was added to 50 mL of ethanol and stirred until clarified, followed by addition of 690.2 mg activated charcoal (DARCO®G-60). Then the mixture was stirred under reflux at 70 °C for 6 h. After ethanol was removed by rotary evaporation, the remaining solid was dried at 80 °C for 12 h. The pyrolysis of the resulting catalyst precursors were performed at different temperatures (600–900 °C) under N<sub>2</sub> atmosphere for 2 h at a rate of 5 °C/min. The as-synthesized materials were labelled as Co–N/C-X-non-acid (X = pyrolysis temperature) while the catalyst without pyrolysis was labelled as Co–N/C-unpyrolysed. Co–N/C-X was prepared by acid leaching of as-synthesized materials in 2 mol/L HCl aqueous solutions at room temperature for 48 h, followed by thoroughly washing with deionized water. Co/C-800 was prepared with the same procedure as Co–N/C-X except for the absence of 1,10-phenanthroline. N/C-800 was also prepared by the same method in the absence of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O.

#### Characterization

Nitrogen sorption isotherms were determined at 77 K using a QuadraSorb SI4 Station. Before testing, samples need to be pretreated at 300 °C in vacuum, and the Brunauer–Emmett–Teller (BET) surface areas of the samples were calculated from the adsorption data. Transmission electron microscopy (TEM). High-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM) images were required from a JEM-2100F microscope and spherical aberration correction technique was further employed. X-ray photoelectron spectroscopy (XPS) analysis of the samples was measured on a Thermo Scientific ESCALAB 250Xi instrument with an Al K $\alpha$  radiation anode (h $\nu$  = 1486.6 eV). The C 1s line (284.6 eV) was used as the reference to correct the binding energies (BEs). Co loadings were determined by inductively coupled plasma spectrometry-optical emission spectrometry (ICP-OES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation), X-ray adsorption

spectroscopy (XAS) at Co K-edge were collected at the BL14W1 at Shanghai Synchrotron Radiation Facility (SSRF), Shanghai institute of applied physics (SINAP), China.

### **Experimental section**

40 mg amount of Co-C/N-800 catalyst (5 mol % Co) were added to a 25 mL flask. Then, 6.9 mg of  $K_2CO_3$  (0.05 mmol), 26.0 mg of styrene (0.25 mmol) and 4 mL of isopropanol were added sequentially. The resulting mixture was transferred to an auto-clave and 0.4 MPa dioxygen was charged. After the reaction, the reactor was placed into an ice bath and cooled to room temperature. Biphenyl was added to the reaction solution as an internal standard. Then, the catalyst was filtered out, and a sample of the mixture was directly subjected to GC analysis. All products were quantitatively and qualitatively analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) and were identified by comparison with authentic samples.

# Catalyst characterizations



Figure S1. SEM images of Co-N/C-600.



Figure S2. SEM images of Co-N/C-700.



Figure S3. SEM images of Co-N/C-800 under LED/UED modes.



Figure S4. SEM images of Co-N/C-800 under BED mode.



Figure S5. SEM images of Co-N/C-800-non-acid.



Figure S6. SEM images of Co-N/C-900.



Figure S7. TEM images of Co-N/C-600.



Figure S8. TEM images of Co-N/C-700.



Figure S9. TEM images of Co-N/C-800.



Figure S10. TEM images of nanoparticles in Co-N/C-800.



Figure S11. TEM images of nanoparticles in Co-N/C-900.



Figure S12. HRTEM images of nanoparticles in Co-N/C-800.



Figure S13. HADDF-TEM images of Co-N/C-800.



Figure S14. N<sub>2</sub> adsorption-desorption of Co-N/C-800 at 77 K.



Figure S15. XPS spectra of Co-N/C-800. (a) N 1s, (b) Co 2p, (c) C 1s, and (d) O 1s.

Five peaks in the N 1s spectrum centered at the binding energy of 398.7 eV, 399.0 eV, 399.9 eV, 400.8 eV and 402.1 eV can be deconvoluted. There were assigned to pyridinic N, Co-Nx, pyrrolic N, graphitic N and oxidized nitrogen, respectively (Figure S15a).<sup>3-5</sup> The N 1s spectrum and C 1s spectrum indicated that N atoms were doped in the Co-N/C-800 and coordinated with Co as expected. The presence of a satellite peak in XPS spectrum of Co  $2P_{3/2}$  (B. E. = 780.5 eV) can be ascribed Co single atoms bonded with N in the graphitic sheets (Figure S15b).<sup>1</sup> According to the report of literature, the peaks of metallic cobalt (B. E. = 777.9 eV) are absence in XPS analysis due to the shielding effect of thick graphitic layers encapsulating the Co particles.<sup>1</sup> The C 1s spectrum shows the existence of four types of carbon species: C=C at 284.6 eV, C=N at 285.7 eV, C-N at 286.6 eV, and O-C=O at 289.2 eV(Figure S15c). Therefore, it can be concluded that the Co species detected by XPS arises mainly from the Co single atoms bonded to N atoms in Co-N/C-800.<sup>3</sup> For the O1s spectrum, the three peaks are ascribed to ketonic C=O groups (531.5 eV), C-O groups (533.1 eV) and N-oxide forms (532.3 eV), respectively.<sup>4</sup>



Figure S16. SEM imagines of recycled catalysts.



Figure S17. XRD patterns of Co-N/C-800.

# **Recovery and reuse of the catalyst**

**Table S1.** Recovery and reuse of Co-N/C-800.



<sup>*a*</sup>Yields were determined by GC using biphenyl as the internal standard.



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# Investigation of mechanism

la la	$\begin{array}{c} \text{catalyst, } \stackrel{i}{\text{PrOH}} \\ \hline 0.4 \text{ MPa O}_2, 150  {}^{\circ}\text{C, 6 h} \\ \hline 2a \end{array}$	H +	Jaa	o J
Entry	Catalyst		$\mathrm{Yield}^{b}(\%)$	
			2a	<b>3</b> a
1	Co/C-800		0	0
$2^d$	N/C-800		0	0
3 <sup>e</sup>	Co/C-800+ N/C-800		0	0
$4^{\mathrm{f}}$	Co(OAc) <sub>2</sub> + N/C-800		0	0
5	Co-N/C-800-unpyrolysed		0	0

**Table S2.** Effect of the composition elements of catalyst on the activity<sup>a</sup>

<sup>*a*</sup>Reaction conditions: 0.25 mmol of styrene, 5 mol % catalyst, 20 mol % K<sub>2</sub>CO<sub>3</sub>, 4 mL <sup>*i*</sup>PrOH, 0.4 MPa O<sub>2</sub>, 6h. <sup>*b*</sup>Conversion and yield were determined by GC using biphenyl as the internal standard. <sup>*c*</sup>Without K<sub>2</sub>CO<sub>3</sub>. <sup>*d*</sup>60mg catalyst. <sup>*e*</sup>5mol % Co/C-800 and 40 mg N/C-800. <sup>*f*</sup>5mol % Co(OAc)<sub>2</sub> and 40 mg N/C-800.



Figure S18. Hot filtration experiment



**Figure S19.** Titration experiment of active sites with KSCN. The amount of KSCN was calculated by content of single atom cobalt and 5 mol% of Co-N/C-800 (40 mg) was added. The effect of the amount of KSCN was investigated.



Figure S20. Kinetic study of the Wacker-type oxidation of styrene



Figure S21. The relationship between the selectivity and amount of KSCN

From the figure, we can see that as the amount of KSCN increases from 0 eqv. to 3 eqv., the selectivity of products decrease from 97.1% to 76.4%. When only a small amount of KSCN binds to the single atom active sites, the single atom active sites still play a major role in the

reaction. Nanoparticles are more involved in the catalysis of side reactions and the selectivity is decreased slightly. When KSCN binds to most of the single atom active sites, that is, the amount of KSCN continues to increase, and the selectivity slightly increases which indicates that the single-atom active site and nanoparticles may play a synergistic role in the catalysis of side reactions, that is, the nanoparticles themselves may not catalyze the occurrence of side reactions alone.

 Table S3. Free radicals capture experiment.

	Co-N/C K <sub>2</sub> CC	C-800 (5 mol%) D <sub>3</sub> (20 mol%)		H \+		o I
1a	Radica <sup>/</sup> PrOH, 0.4 N	al scavenger ⁄Ipa O <sub>2</sub> , 150 °C, 6 h	2a		3a	
	Radical trap	rad trap/catal *		Yıeld	(%)	
	1	-		2a	<b>3</b> a	
	No scavenger	-		1.2	95.8	
	TEMPO	1.2		10.3	55.2	
	BHT	1.2		12.7	38.2	
	BHT	2		10.2	24.6	
	AM	1.2		10.0	63.2	



Scheme S1. Control experiments

## The proposed reaction process



Scheme S2. The proposed reaction process.

#### Notes and references

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