Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

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**

[a] State Key Laboratory of Heavy oil Processing, China University of Petroleum (Beijing), Beijing 102249, China

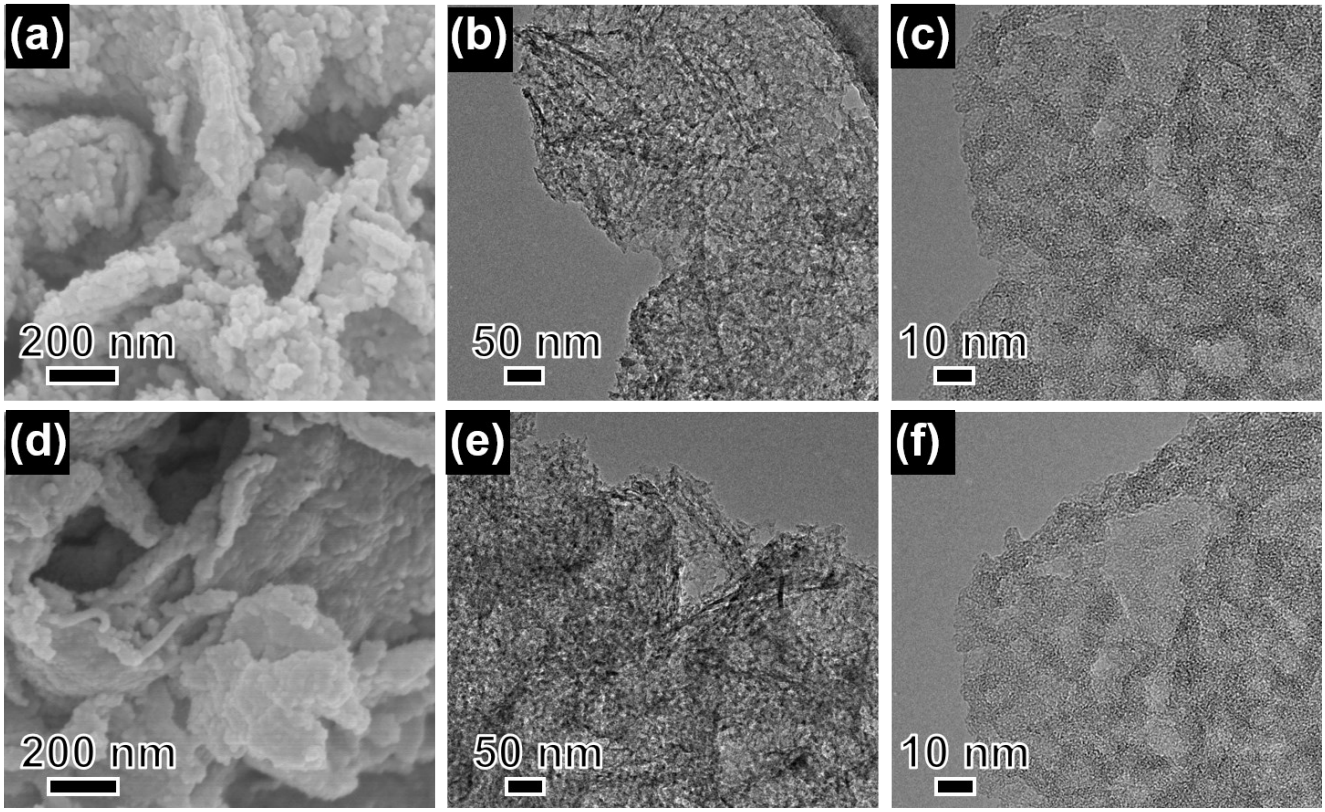


Fig. S1. (a) SEM image, (b, c) TEM images of Co-N-C-700. (d) SEM image, (e, f) TEM images of Co-N-C-900

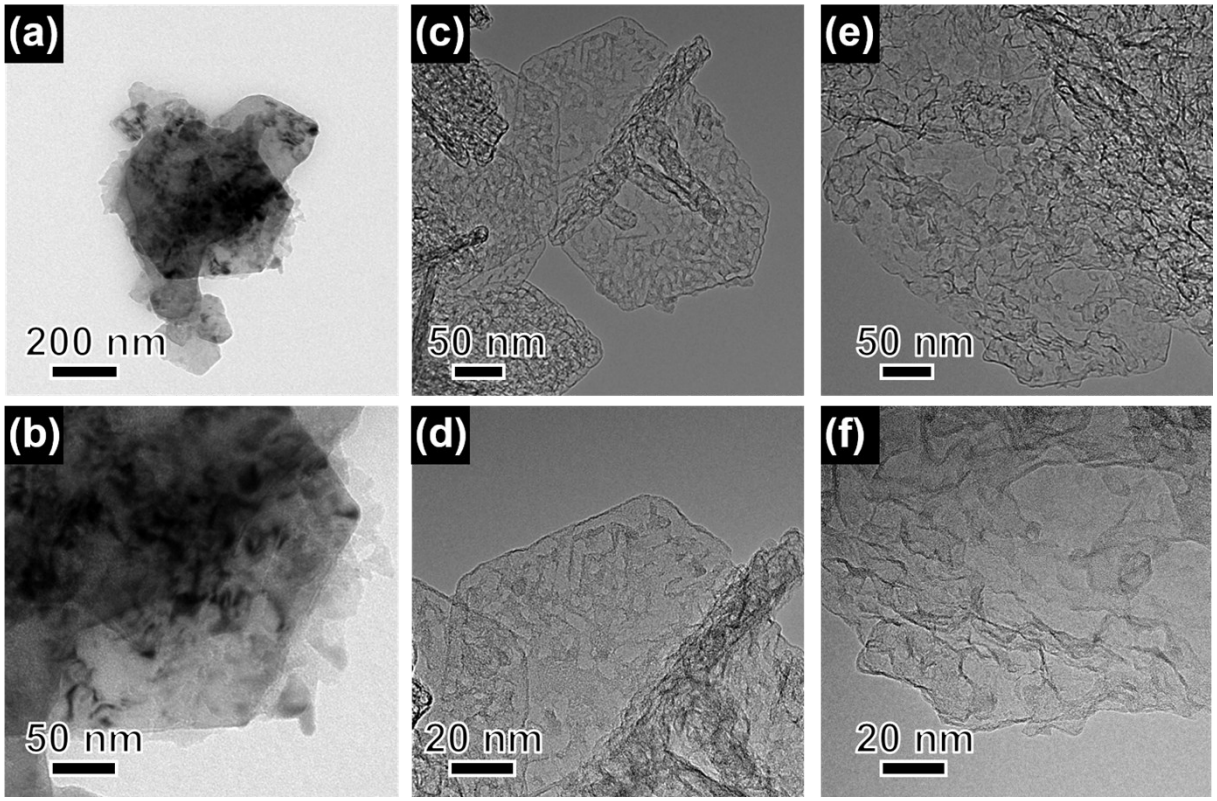


Fig. S2. TEM images of Co-N-C-MgO (a, b), NPC (c, d) and Co-PC (e, f).

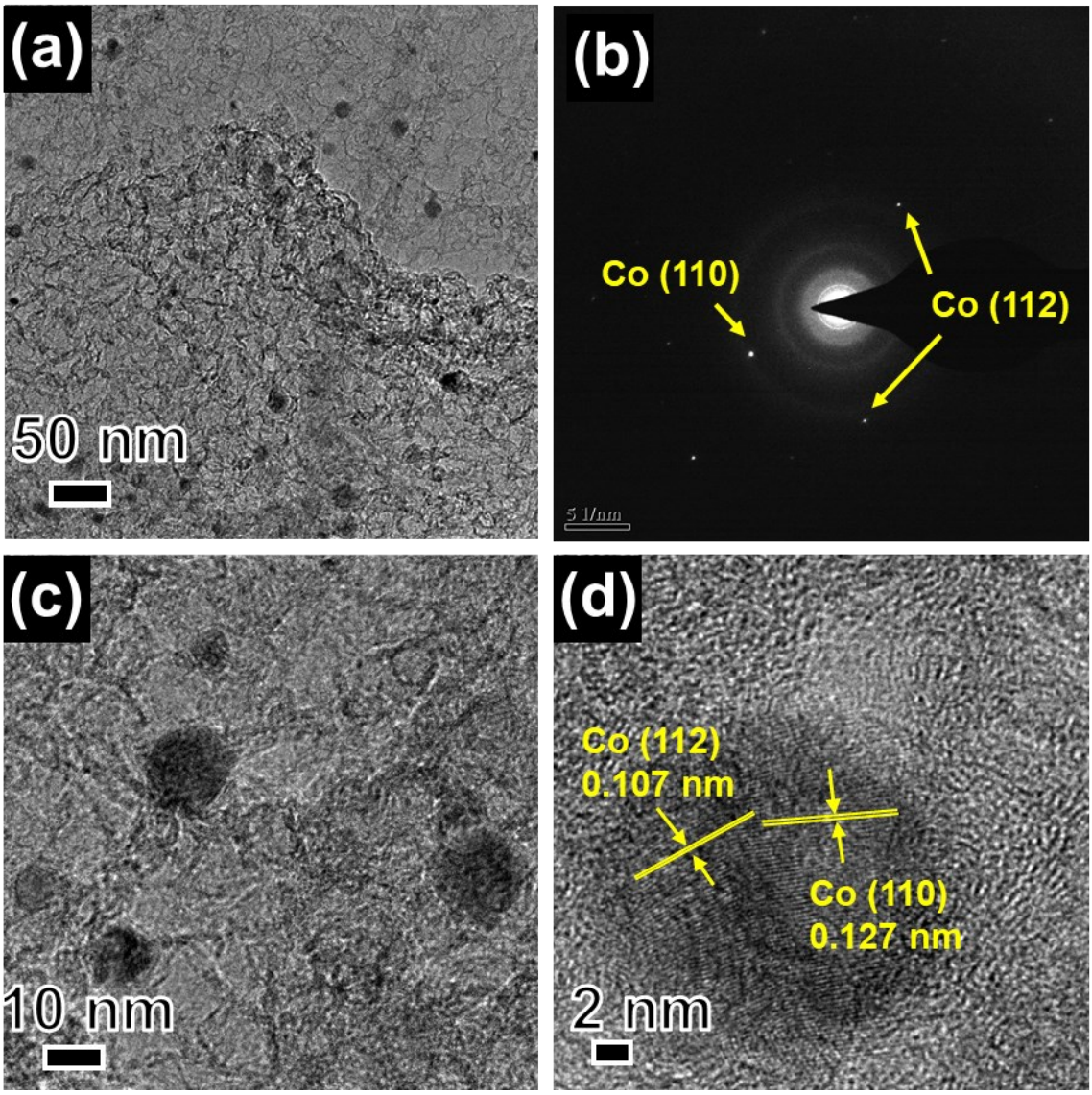


Fig. S3. TEM images of Co NC and the corresponding SAED pattern (b).

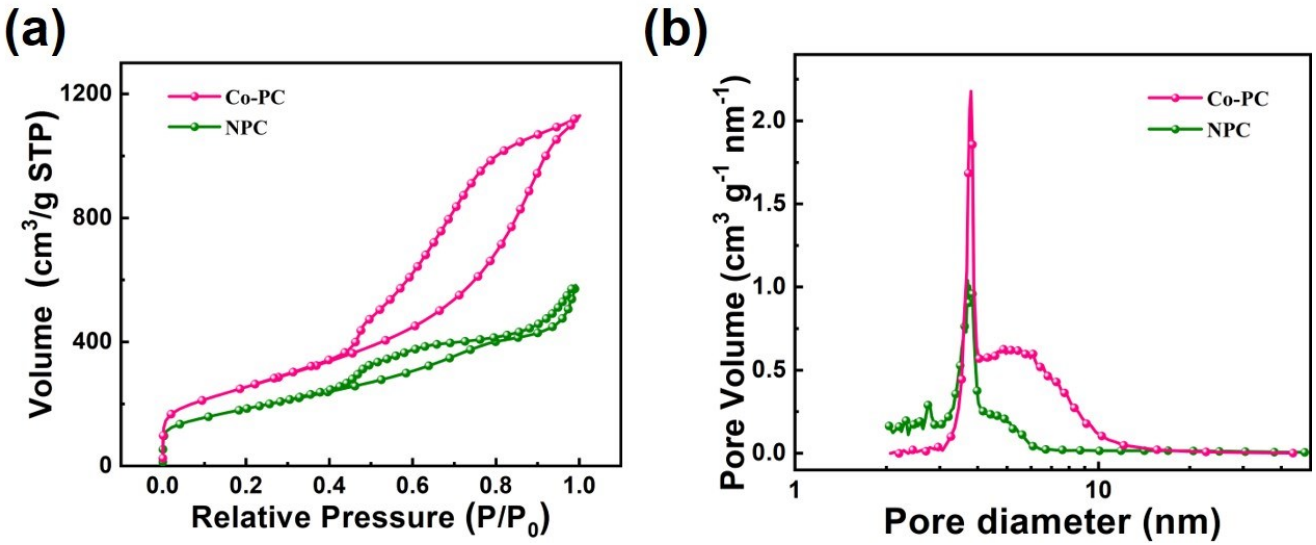


Fig. S4. Nitrogen sorption isotherms (a) and pore size distribution (b) of NPC and Co-PC.

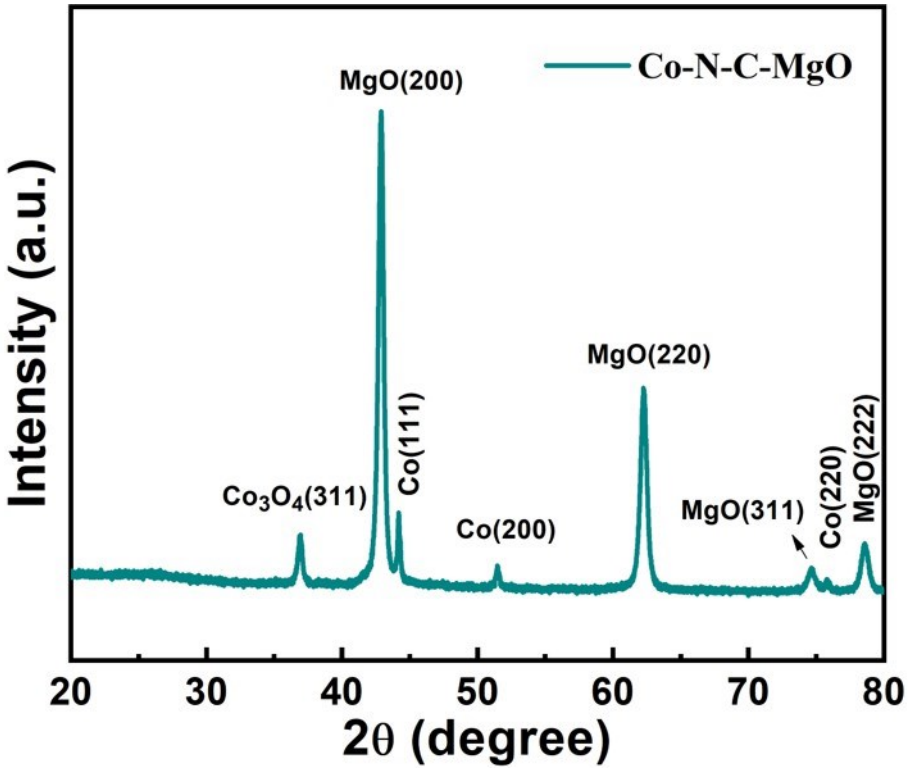


Fig. S5. XRD of Co-N-C-MgO

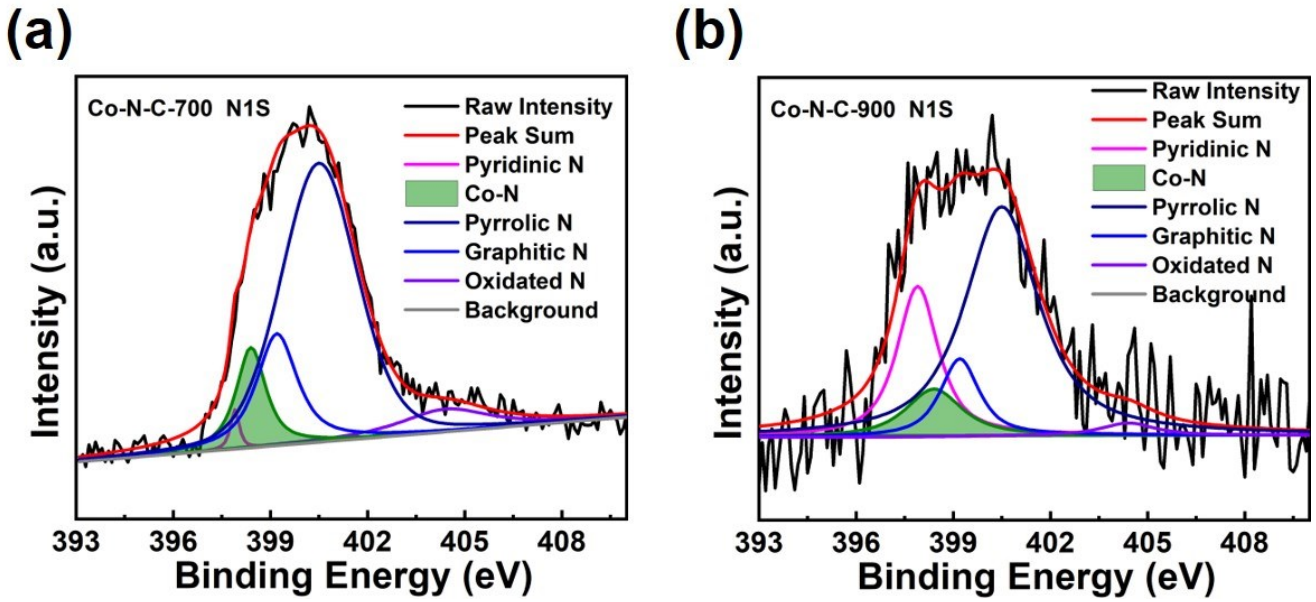


Fig. S6. XPS N 1s spectra of (a) Co-N-C-700 and (b) Co-N-C-900

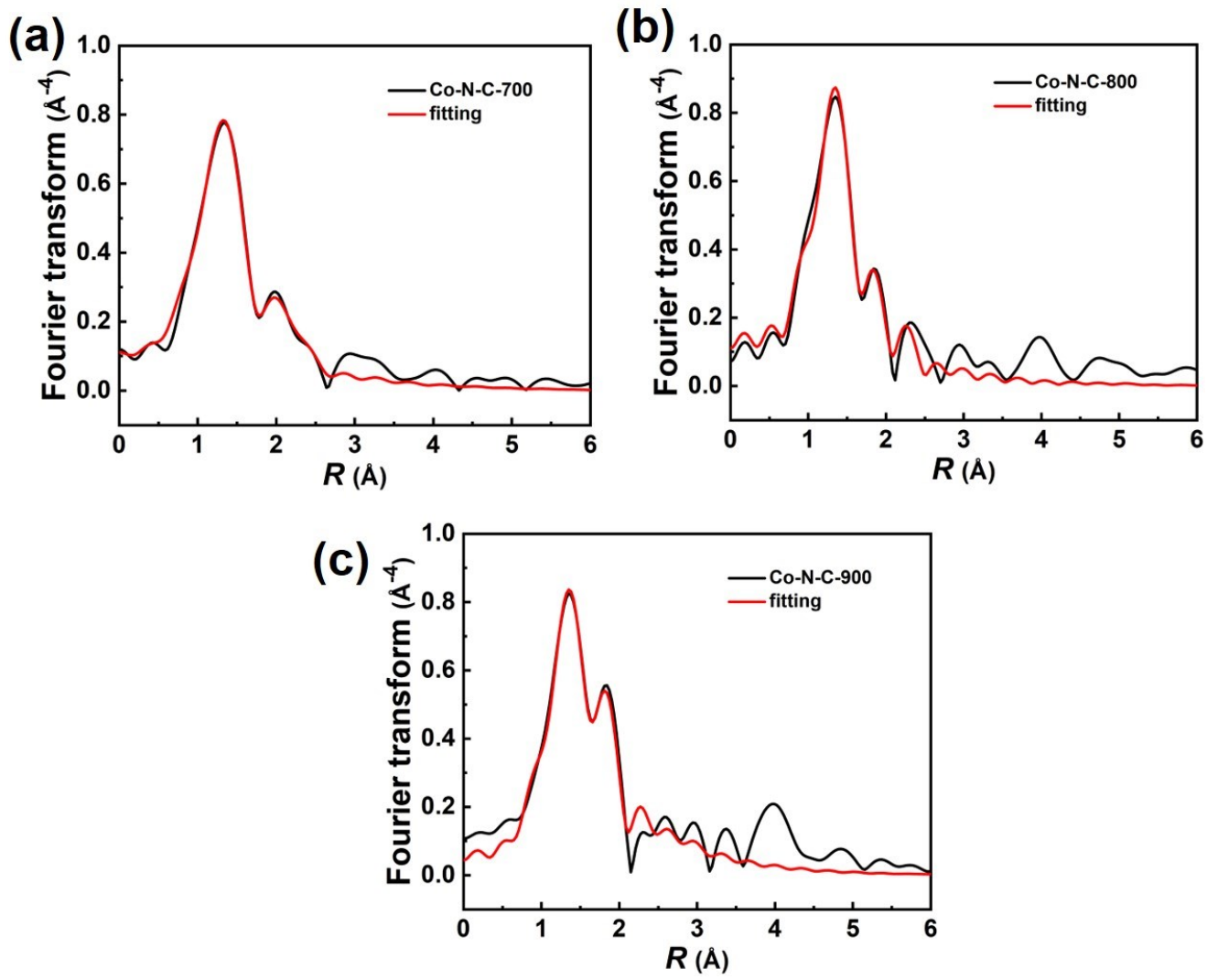


Fig. S7. The corresponding EXAFS fitting curves of (a) Co-N-C-700, (b) Co-N-C-800 and (c) Co-N-C-900.

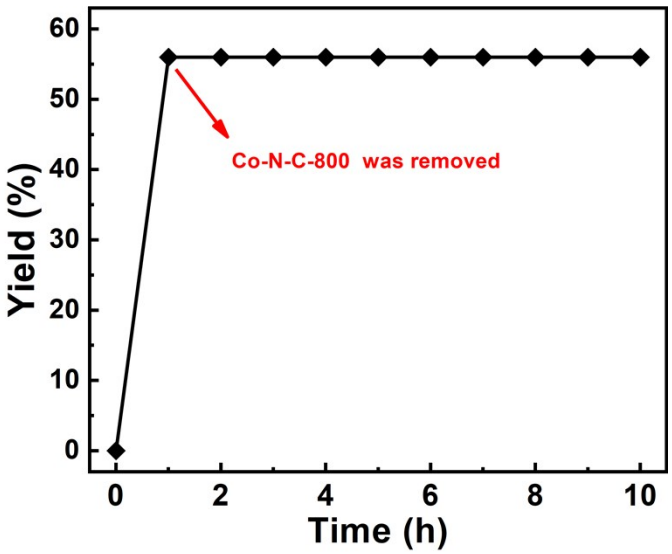


Fig. S8. Evaluation of Co leaching during dimethylphenylsilane oxidation by Co-N-C-800.

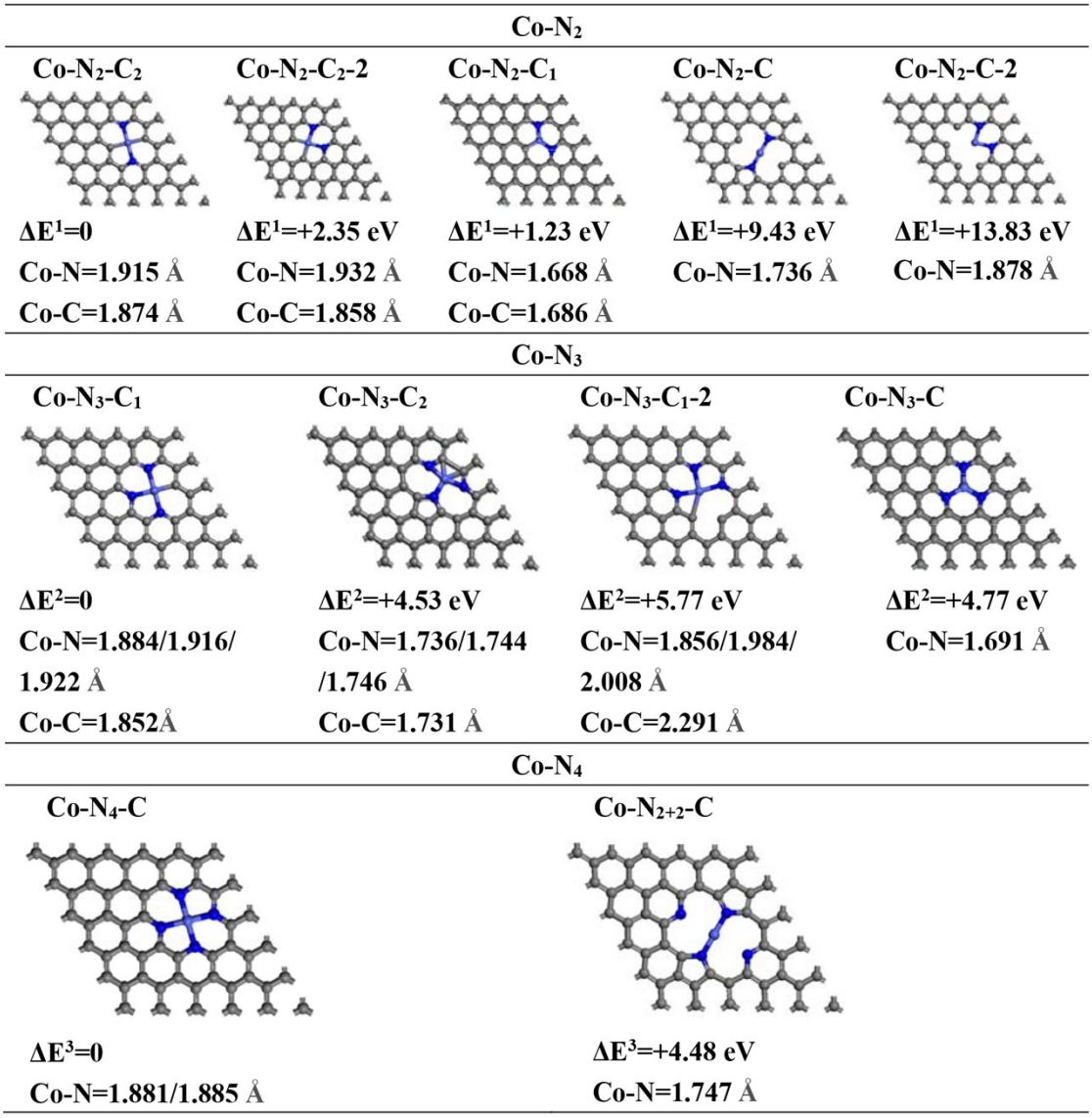


Fig. S9. Possible models of Co-N_x (x=2-4). The gray, blue and light blue balls stand for carbon, nitrogen, and cobalt atoms, respectively.

*1:$\Delta E=E_{Co\text{-}Nx\text{-}Cy}-E_{GNx}-E_{Co}-E_{Co\text{-}N2\text{-}C2}$; *2:$\Delta E=E_{Co\text{-}Nx\text{-}Cy}-E_{GNx}-E_{Co}-E_{Co\text{-}N3\text{-}C1}$; *3:$\Delta E=E_{Co\text{-}Nx\text{-}Cy}-E_{GNx}-E_{Co}-E_{Co\text{-}N4\text{-}C}$

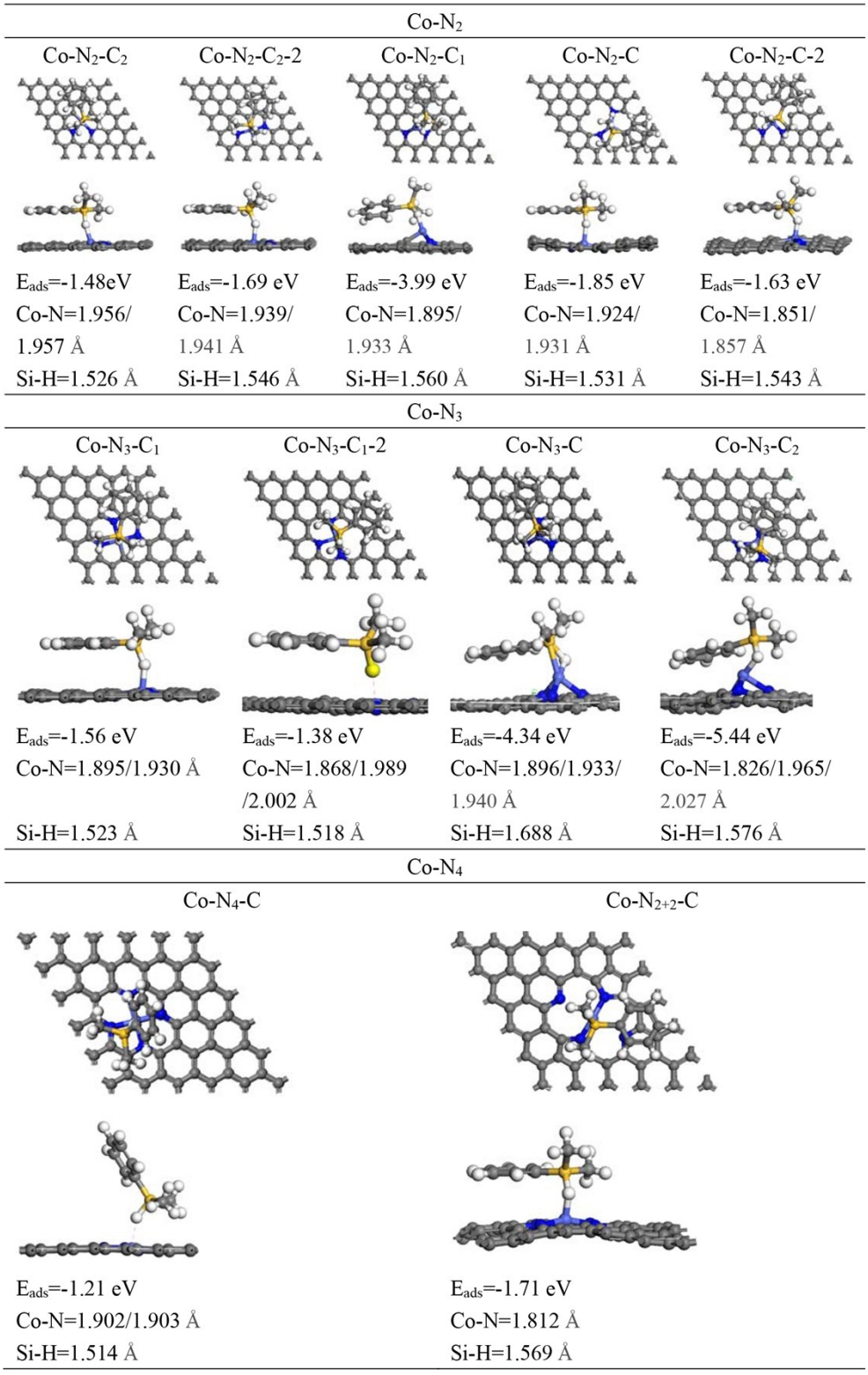


Fig. S10. Adsorption structures of dimethylphenylsilane on Co-N_x substrates

Among them, configurations Co-N_2-C_1 of Co-N_2, Co-N_3-C and Co-N_3-C_2 of Co-N= and Co-N_{2+2}-C of Co-N_4 were energetically favored ones. As expected, the adsorption strength of substrates with four-fold coordination of Co atom were usually less than that of unsaturated ones, and showing less activation of Si-H bond, compared with the bond length of Si-H of dimethylphenylsilane in gas phase (1.496 Å).

Table S1. The elemental compositions of catalysts estimated from XPS

Sample	C (at %)	O (at %)	N (at %)	Co (at %)	Co (wt %)
Co-N-C-700	80.79	20.51	8.24	0.46	2.1
Co-N-C-800	83.41	7.58	8.46	0.55	2.5
Co-N-C-900	86.54	6.31	6.71	0.44	2.1

[a] C, O, N and Co contents were detected by XPS; [b] Co contents were calculated based on the contents of C, N, O and Co.

Table S2. The total nitrogen content and percentage of different nitrogen species in Co-N-C catalysts

Sample	N (at %)	Pyridinic N	Co-N	Pyrrolic N	Graphitic N	Oxidized N
Co-N-C-700	8.24	0.11	0.91	1.40	5.20	0.62
Co-N-C-800	8.46	1.82	0.81	0.98	3.00	1.85
Co-N-C-900	6.71	1.42	0.61	0.68	3.85	0.15

[a] It was calculated according to the peak area of different types of N.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples

Sample	Shell	N [a]	R (Å) [b]	σ^2 ($Å^2 \cdot 10^3$) [c]	ΔE_0 (eV) [d]	R factor (%)
Co-N-C-700	Co-N	0.85*4.1	1.88	9.0	5.1	0.3
Co-N-C-800	Co-N	0.85*3.6	1.88	2.9	7.2	0.8
Co-N-C-900	Co-N	0.85*2.2	1.83	3.7	2.1	1.0

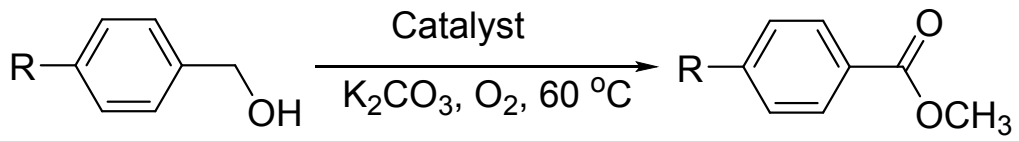
[a] N: coordination numbers. [b] R: bond distance. [c] σ2: Debye-Waller factors. [d] ΔE0: the inner potential correction. [e] R factor: goodness of fit. S02, 0.85, was obtained from the experimental EXAFS fit of CoPc reference by fixing CN as the known crystallographic value and was fixed to all the samples.

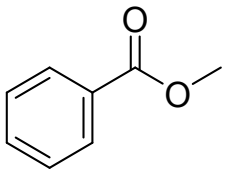
Table S4. Comparation of oxidation of organosilane to silanol between Co-N-C-800 and other catalysts in literature.

Entry	Catalyst	Oxidant	Temp. /°C	Time /h	TOF /h^{-1}	Yield /%	Ref.
1	**Co-N-C-800**	**H_2O**	**Room Temp.**	**1.8**	**381**	**97**	**This work**
2	Single-Site Au	H_2O	Room Temp.	0.5	50200	99	*Adv. Mater.* **2018**, *30*, 1704720.[1]
3	Pd/XC-72-700-Ar	H_2O	Room Temp.	57 s	645300	>99	ACS Catal. **2017**, 7, 1720-1727.[2]
4	Pd/MgO catalyst	H_2O	Room Temp.	2	300	85	Catalysts **2019**, 9, 834.[3]
5	Au nanoparticles	H_2O	45	22	(TON) 591000	100	J. Mater. Chem. A, **2017**,5, 1935-1940.[4]
6	$Cu_3(BTC)_2$	TBHP	60	20	-	99	Appl. Catal. A-Gen 544 **2017**,145-153.[5]
7	Nanoporous copper	H_2O	Room Temp.	2	-	92	ChemPhysChem **2015**, 16, 1603-1606.[6]
8	NaY zeolite	85% H_2O_2	80	0.07	-	99	J. Org. Chem. **2000**, 65, 2897-2899.[7]
9	Ni powder	H_2O	110	20	6.4	85	J. Mol. Catal. A: Chem., **2012**, 365, 50-54.[8]
10	TC-6 (Ir homogeneous catalyst)	H_2O	Room Temp.	6	-	95	Organometallics **2020**, 39, 165−171.[9]

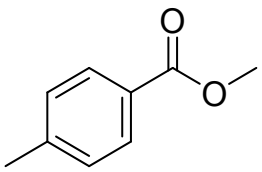
11	$Mn(ClO_4)_2 \cdot 6H_2O$	H_2O_2	Room Temp.	1	99		Angew. Chem. **2019**, 131, 6446-6450.[10]
12	Lacunary polyoxotungstate	H_2O_2	60	2	-	99	Angew Chem Int Ed Engl, **2009**, 48, 8900-8904.[11]

Table S5. Co-N-C-800 catalyzed the esterification of benzyl alcohol[a]

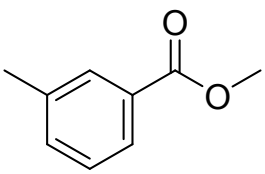




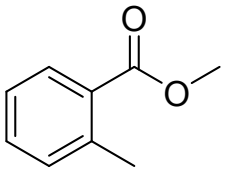
1, 92 %



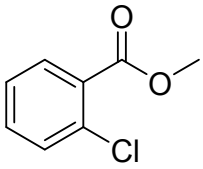
2, 97 %



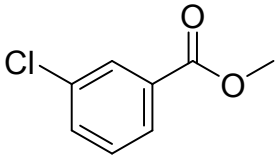
3, 95%



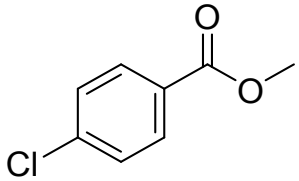
4, 91%



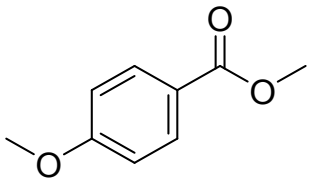
5, 90%



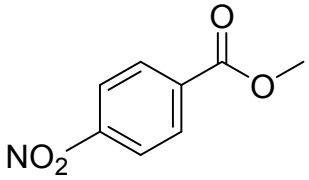
6, 92%



7, 94 %



8, 98 %



9[b], 87 %

[a] Reaction conditions: 0.4 mmol benzylic alcohol, 10 mg Co-N-C-800 catalyst, 0.08 mmol K_2CO_3 in 3 mL CH_3OH, O_2 (1 atm), 12 h. [b] Reaction conditions: 0.4 mmol benzylic alcohol, 10 mg Co-N-C-800 catalyst, 0.08 mmol K_2CO_3 in 3 mL CH_3OH, O_2 (1 atm)，20 h. [c] Isolated yield.

References

(1) Z. Chen, Q. Zhang, W. Chen, J. Dong, H. Yao, X. Zhang, X. Tong, D. Wang, Q. Peng, C. Chen, W. He and Y. Li, *Adv. Mater.*, 2018, **30**, 1704720.

(2) J. D. Lin, Q. Y. Bi, L. Tao, T. Jiang, Y. M. Liu, H. Y. He, Y. Cao and Y. D. Wang, ACS Catal., 2017, **7**, 1720-1727.

(3) J. Zhou, X. Cao, H. Wang and S. Li, *Catalysts*, 2019, **9**, 834.

(4) M. Dhiman, B. Chalke and V. Polshettiwar, *J. Mater. Chem. A*, 2017, **5**, 1935-1940.

(5) N. Anbu and A. Dhakshinamoorthy, *Appl. Catal. A-Gen.*, 2017, **544**, 145-153.

(6) Z. Li, X. Xu and X. Zhang, *ChemPhysChem*, 2015, **16**, 1603-1606.

(7) W. Adam, C. R. Saha-Möller and O. Weichold, *J. Org. chem.*, 2000, **65**, 2897-2899.

(8) K.-i. Shimizu, K. Shimura, N. Imaiida and A. Satsuma, *J. Mol. Catal. A: Chem.*, 2012, **365**, 50-54.

(9) N. Luo, J. Liao, O. Lu, H. Wen, Y. Zhong, J. Liu, W. Tang and R. Luo, *Organometallics*, 2019, **39**, 165-171.

(10) W. Kaikai, Z. Jimei, J. Yuting, Z. Miaomiao, W. Chao, X. Dong, T. Weijun, S. Huamin, X. Jianliang and L. Chaoqun, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 6380-6384.

(11) IRyo, K. Keigo and M. Noritaka, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 8900-8904.