Supplementary Information

Highly-selective oxidation of benzyl alcohol to benzaldehyde over Co_1/NC catalysts

Fan Xue [a], *Yanle Li* [b], *Jingyue Bi* [a], *Shangpu Zhuang* [a], *Mifen Cui* [a], *Zhaoyang Fei* [*, a], *Ziqi Tian* [*, b] *and Xu Qiao* [*, a]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu, 211816, PR China

[b] Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, PR China

* E-mail: tianziqi@nimte.ac.cn (Z. Tian).

* E-mail: zhaoyangfei@njtech.edu.cn (Z. Fei), Tel: +86 025 83587168, Fax: +86 025 83587168.

* E-mail: qct@njtech.edu.cn (X. Qiao), Tel: +86 025 83172298, Fax: +86 025 83172298.

Summary of the supporting information: 11 pages, 12 figures and 4 tables.

Table of Contents

Chemicals

Reagents zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O \geq 99$ %), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O > 99$ %), 2-methylimidazole (2-HMIM > 99%), 4-Bromobenzyl alcohol (≥ 99 %), 3-Bromobenzyl alcohol (≥ 99 %), 2-Bromobenzyl alcohol (≥ 99 %), 4-Chlorobenzyl alcohol (≥ 99 %), (S)-(-)-1-Phenylethanol (≥ 99 %), 4-Hydroxybenzyl alcohol (≥ 99 %) and Diphenylmethanol (≥ 99 %) were purchased from Shanghai Aladdin Biochemical Technology Co.. P-Tolymethanol (98.78 %) was purchased from Bidephatm com. Methanol (> 99.5 %), N, N-dimethylformamide (DMF, > 99.5 %), benzaldehyde (> 99.5 %), benzyl alcohol (> 99.5 %) and benzoic acid (> 99.5 %) were bought from Taicang Shanghai Trial Agent Co., Ltd, China. All the chemicals were analytical pure grade and used without further purification.

DFT calculations

The Co atom in 4-Co_1/NC catalyst was surrounded by four nitrogen atoms and Co NPs in Co_{NPs}/NC catalyst was represented by a Co_6 cluster as reported. [1] The benzyl alcohol oxidation process was studied by calculating the energy changes of the following four reactions: [2]

$$*Ph\text{-}CH_2OH@O_2\text{-}Co_x/NC \rightarrow *Ph\text{-}CHO@O_1\text{-}Co_x/NC + H_2O \quad (1)$$

$$*Ph\text{-}CHO@O_1\text{-}Co_x/NC \rightarrow Ph\text{-}CHO + *O_1\text{-}Co_x/NC \quad (2)$$

$$*Ph\text{-}CH_2OH@O_1\text{-}Co_x/NC \rightarrow *Ph\text{-}CHO@Co_x/NC + H_2O \quad (3)$$

$$*Ph\text{-}CHO@Co_x/NC \rightarrow Ph\text{-}CHO + *Co_x/NC \quad (4),$$

where the asterisk and @ denote to the adsorption states at different stages and Co_x/NC represents 4-Co_1/NC or Co_{NPs}/NC catalyst.

Figures

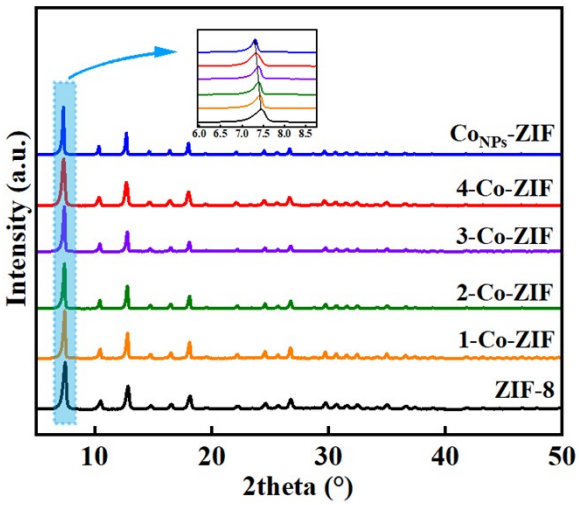

Fig. S1 XRD patterns of Co-ZIF precursors.

The main peak of Co-ZIF precursors shifted slightly to a smaller angle compared with the pristine ZIF-8, indicating that the Co^{2+} ions partially substituted the Zn^{2+} ions.

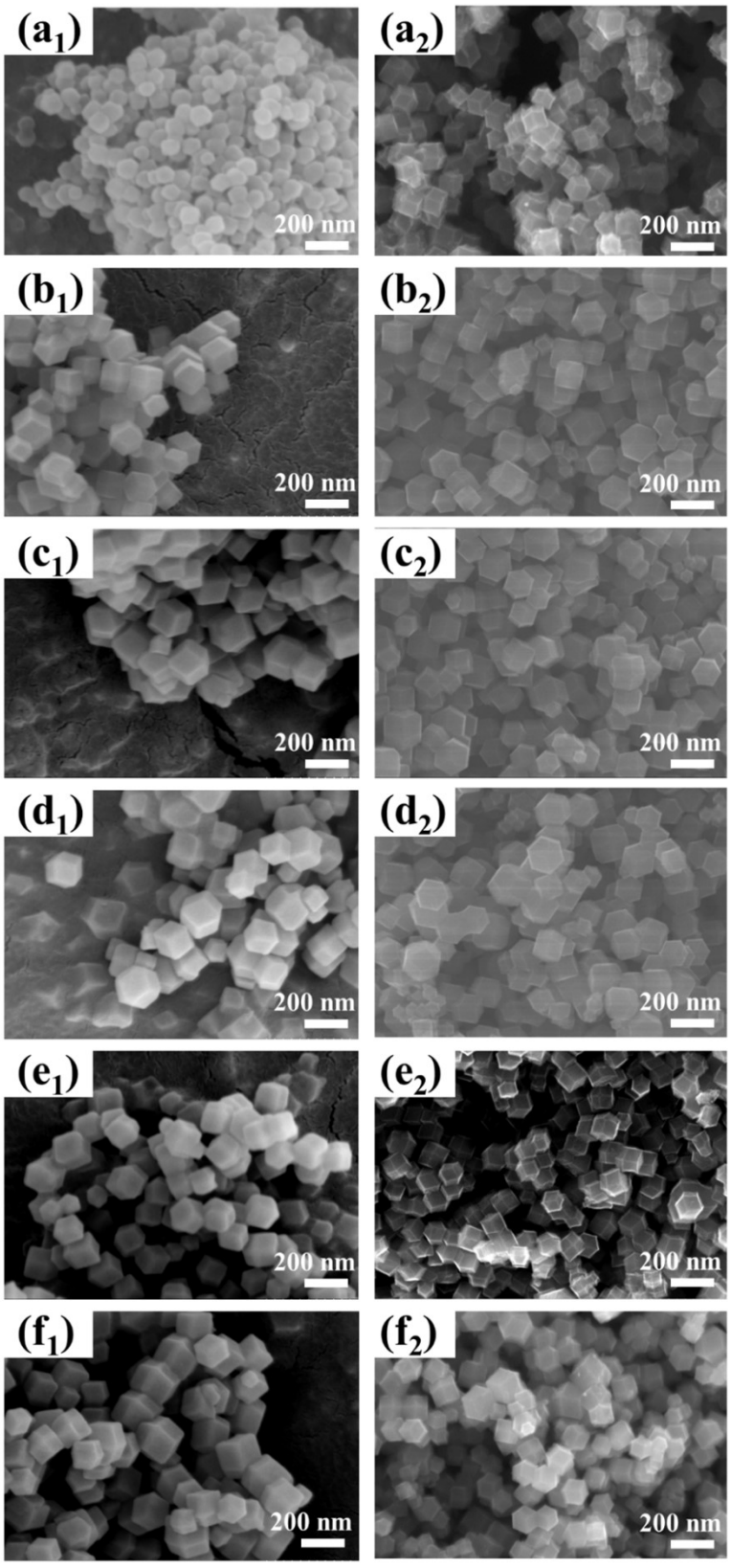

Fig.S2 Typical SEM images of (a_1) ZIF-8, (a_2) NC, (b_1) 1-Co-ZIF, (b_2) 1-Co_1/NC, (c_1) 2-Co-ZIF, (c_2) 2-Co_1/NC, (d_1) 3-Co-ZIF, (d_2) 3-Co_1/NC, (e_1) 4-Co-ZIF, (e_2) 4-Co_1/NC, (f_1) Co_{NPs}-ZIF, (f_2) Co_{NPs}/NC.

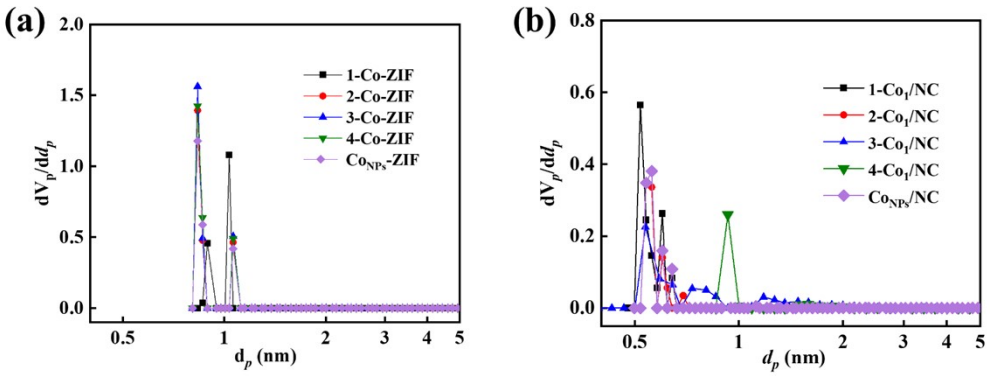

Fig.S3 The pore size distributions of the (a) precursors and (b) catalysts.

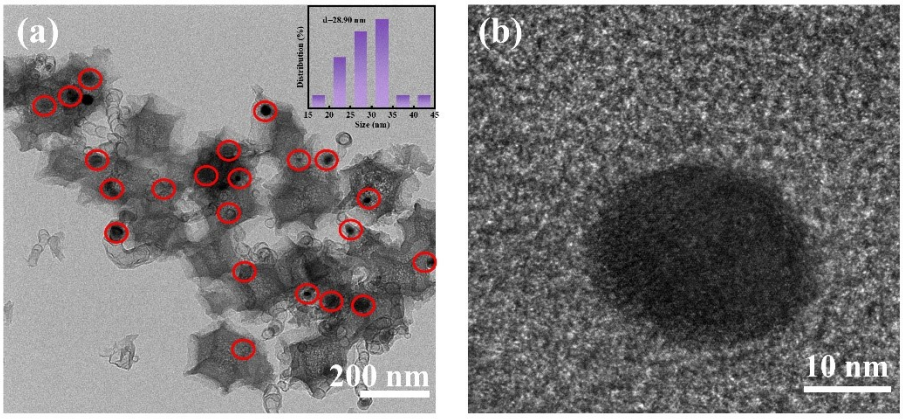

Fig.S4 (a) TEM image and (b) HRTEM image of Co_{NPs}/NC catalyst.

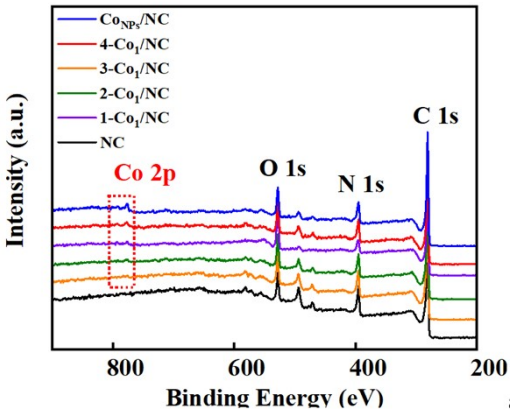

Fig.S5 The XPS spectra of Co_1/NC and Co_{NPs}/NC catalysts.

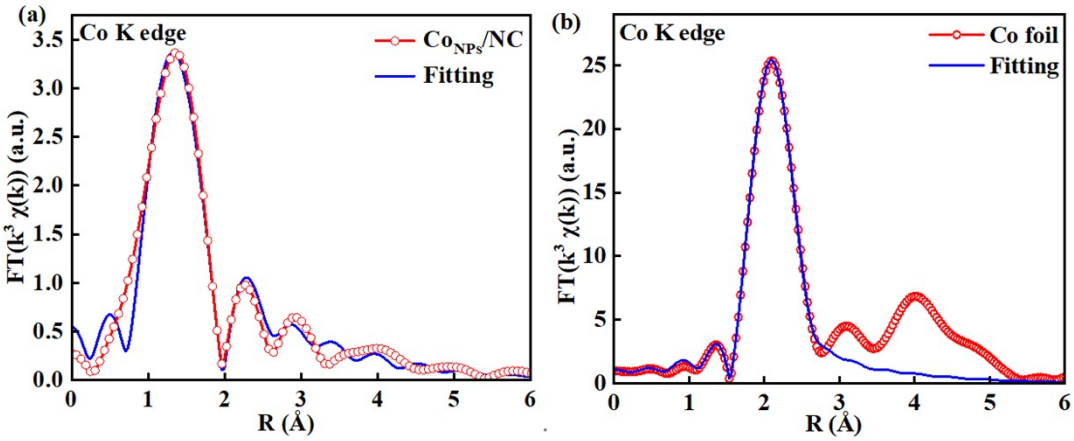

Fig.S6 The Co K edge FT-EXAFS spectrum and corresponding fitting curve in R space for (a) Co_{NPs}/NC and (b) Co foil.

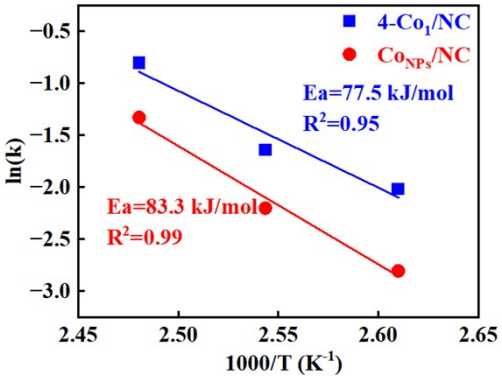

Fig.S7 Ea value of 4-Co_1/NC and Co_{NPs}/NC catalysts.

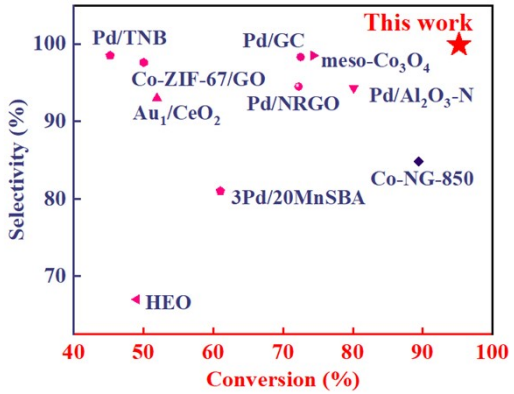

Fig.S8 Comparison of the catalytic conversion of 4-Co_1/NC catalyst with those reported previously (Co-ZIF-67/GO [3], Pd/GC [4], Au_1/CeO_2 [5], Pd/NRGO [6], 3Pd/20MnSBA [7], HEO [8], meso-Co_3O_4 [9], Pd/TNB [10], Pd/Al_2O_3-N [11], Co-NG-850 [12].

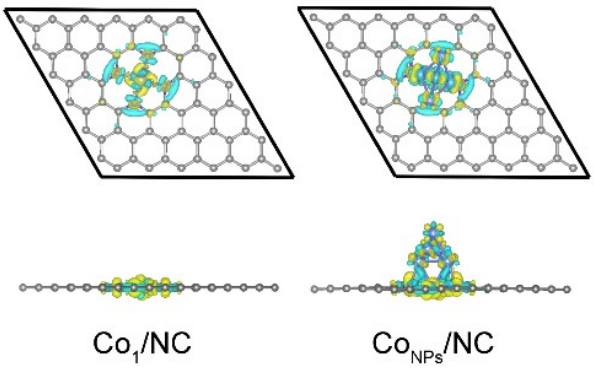

Fig.S9 Charge density difference of Co_1/NC and Co_{NPs}/NC models. The isosurface level is 0.006 eÅ^{-3}. Yellow and cyan regions represent the accumulation and depletion of electrons.

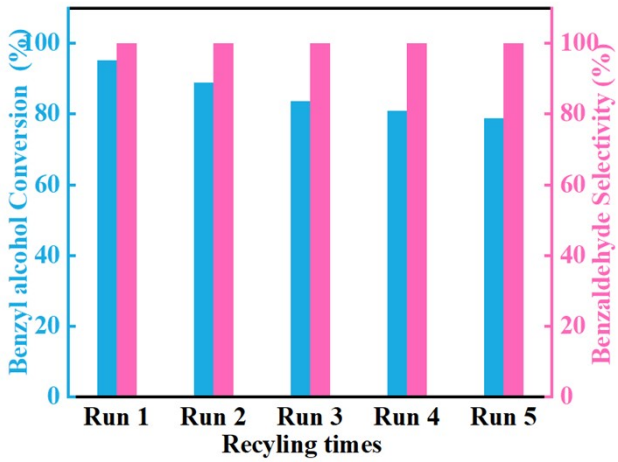

Fig.S10 Recycling results of 4-Co_1/NC catalyst.

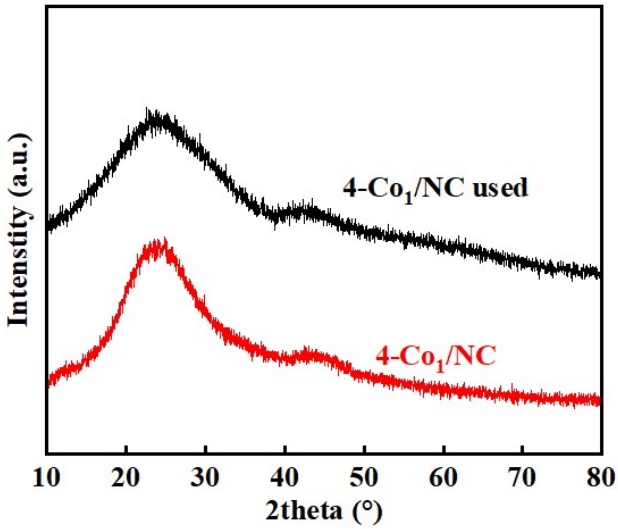

Fig.S11 The XRD patterns of the fresh and used 4-Co_1/NC catalysts.

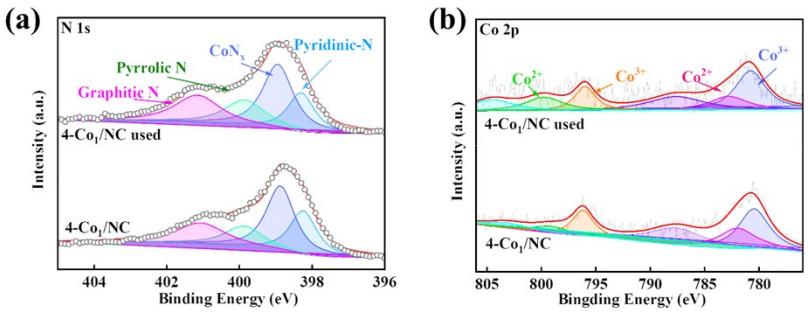

Fig.S12 (a) the N 1s and (b) Co 2p spectra of the fresh and the used 4-Co_1/NC catalysts.

Tables

Table.S1 Co contents measured by ICP-AES.

Catalysts	Metal loading (wt %)
1-Co_1/NC	0.8
2-Co_1/NC	1.4
3-Co_1/NC	1.6
4-Co_1/NC	2.3
Co_{NPs}/NC	3.6

Table.S2 Textural parameters of the catalysts.

Catalysts	S_{BET} ($m^2 \cdot g^{-1}$) [a]	N (%)	Co/N	N 1s				Co 2p
				Pyridinic N (%)	Co-N (%)	Pyrrolic N (%)	Graphitic N (%)	Co^{3+}/Co^{2+}
1-Co_1/NC	688	12.0	0.067	31.1	28.5	16.1	24.3	2.48
2-Co_1/NC	647	12.1	0.116	25.8	32.2	16.1	25.9	1.73
3-Co_1/NC	787	12.2	0.131	19.9	35.4	18.8	25.9	1.71
4-Co_1/NC	908	11.6	0.198	24.4	37.8	16.4	21.3	1.63
Co_{NPs}/NC	524	12.3	0.293	32.0	26.9	18.0	23.1	2.24

a Calculated by BET method

Table.S3 FT-EXAFS fitting results at the Co K-edge

Samples	Shell	C.N [a]	R (Å) [b]	σ^2 [c]	$\triangle E_0$ (eV) [d]	R factor (%) [e]
Co foil	Co-Co	12*	2.49	0.0053	-3.7	0.0037
4-Co_1/NC	Co-N	3.9	2.03	0.0163	-8.5	0.0078
Co_{NPs}/NC	Co-N	3.9	2.04	0.0143	-6.7	0.0209
	Co-Co	12.0	2.56	0.0723	-6.7	0.0209

[a] C.N: coordination numbers

[b] R: bond distance

[c] σ^2: Debye-Waller factors

[d] ΔE: the inner potential correction

[e] R factor: goodness of fit.

* The experimental EXAFS fit of metal foil by fixing CN as the known crystallographic value. The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k^3 weighting, k range of 0-12 $Å^{-1}$ and R range of 1-2 Å were used for the fitting. The four parameters, coordination number, bond length, and E_0 shift (CN, R, ΔE_0) were fitted without anyone was fixed, constrained, or correlated while the σ^2 was set.

Table.S4 Comparison of different catalysts in the oxidation of benzyl alcohol

Catalysts	Solvent	T (°C)	t (h)	Conversion (%)	Selectivity (%)
Co-ZIF-67/GO[3]	DMF	100	8	50	97.6
Pd/GC[4]	——	110	6	72.5	98.3
Au_1/CeO_2[5]	——	150	8	51.9	93
Pd/NRGO[6]	——	90	3	72.2	94.5
3Pd/20MnSBA[7]	——	90	7.5	61	81
HEO[8]	——	120	0.5	49	67
meso-Co_3O_4[9]	DMF	120	6	74.3	98.5
Pd/TNB[10]	——	120	1	45.2	98.5
Pd/Al_2O_3-N[11]	——	120	8	80.1	94.3
Co-NG-850[12]	DMF	130	5	89.4	84.8
Au-SA/CeO_2-NR[13]	Toluene	100	24	89	94

References

1. P. E. Blöchl, Phys. Rev. B., 1994, **50**, 17953-17979.
2. K. T. Huang, H. Q. Fu, Wen Shi, H. J. Wang, Y. H. Cao a, G. X. Yang, F. Peng , Q. Wang, Z. G. Liu, B. S. Zhang and H. Yu, J. Catal. 2019, **377**, 283-292.
3. X. Yang, S. Wu, J. Hu, F. R. Xiao, P. Ling, K.B. Qiu, H. S. Qi and G. Q. Jing, Catal. Commun., 2016, **87**, 90-93.
4. G. Wu, X. Wang, N. Guan and L. Li, Appl. Catal. B., 2013, **136-137**, 177-185.
5. T. Li, F. Liu, Y. Tang, L. Li, S. Miao, Y. Su, J. Y. Zhang, J. H. Huang, H. Sun, M. Haruta, A. Q. Wang, B. T. Qiao, J. Li ang T. Zhang, Angew. Chem. Int. Ed., 2018, **57**, 7795-7799.
6. Q. Wei, T. Liu, Y. Wang and L. Dai, RSC. Adv., 2019, **9**, 9620-9628.
7. Y. Li, A. Chatterjee, L. B. Chen, FL-Y. Lam and X. Hu, Mol. Catal. 2020, **488**.
8. D. Y. Feng, Y. B. Dong, L. L. Zhang, X. Ge, W. Zhang, S. Dai and Z. A. Qiao, Angew. Chem. Int. Ed., 2020, **59**, 19503-19509.
9. Q. Zhang, X. Fu, Q. Kan and J. Guan, Ind. Eng. Chem. Res., 2019, **58**, 4774-4779.
10. Y. M. Lu, H. Z. Zhu, J. W. Liu and S. H. Yu, ChemCatChem., 2015, **7**, 4131-4136.
11. X. Wang, G. Wu, N. Guan and L. Li, Appl. Catal. B., 2012, **115-116**, 7-15.
12. M. Li, S. J. Wu, X. Y. Yang, J. Hu, L. Peng, L. Bai, Q. S. Huo and J. Q. Guan, Appl. Catal. A-Gen., 2017, **543**, 61-66.
13. L. J. Lei, H. Liu, Z. W. Wu, Z. F. Qin, G. F. Wang, J. Y. Ma, L. Luo, W. B. Fan and J. G. Wang, ACS. Appl. Nano. Mater., 2019, **2**, 5214-5223.