Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Hydrogenation of CO_2 into aromatics over ZnZrO-Zn/HZSM-5 composite catalysts derived from ZIF-8

Haifeng Tian[a,*], Jiapeng Jiao[a], Fei Zha[a,*], Xiaojun Guo[a], Xiaohua Tang[a], Yue Chang[a, b] Hongshan Chen[c]

[a] *College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China*

[b] *Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, Lanzhou 730070, Gansu, China*

c College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China

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[*] Corresponding Author

Haifeng Tian, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China.

Email: thfnwnu@163.com

Fei Zha, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China.

Email: zhafei@nwnu.edu.cn

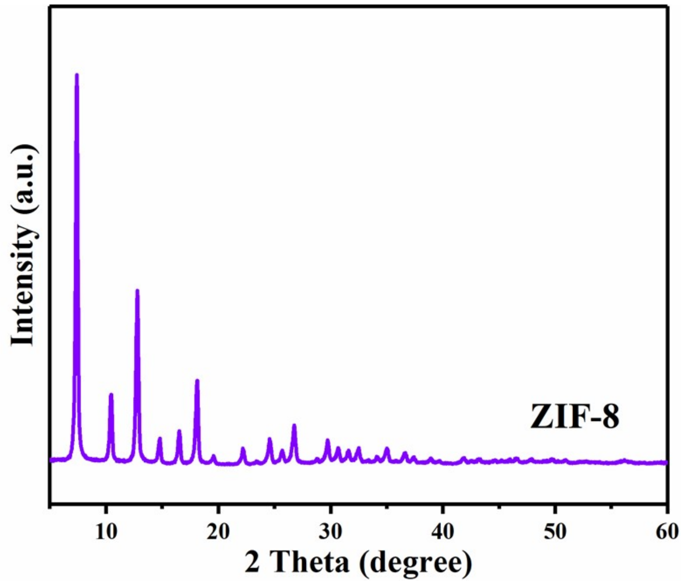

Fig. S1 XRD patterns of ZIF-8.

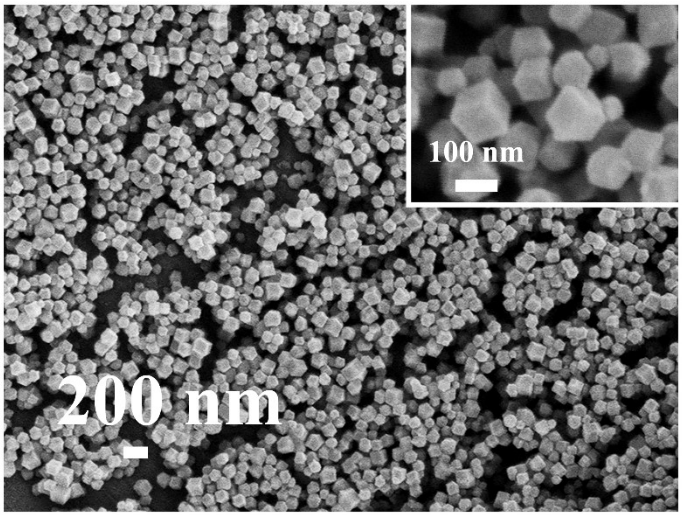

Fig. S2 SEM images of ZIF-8.

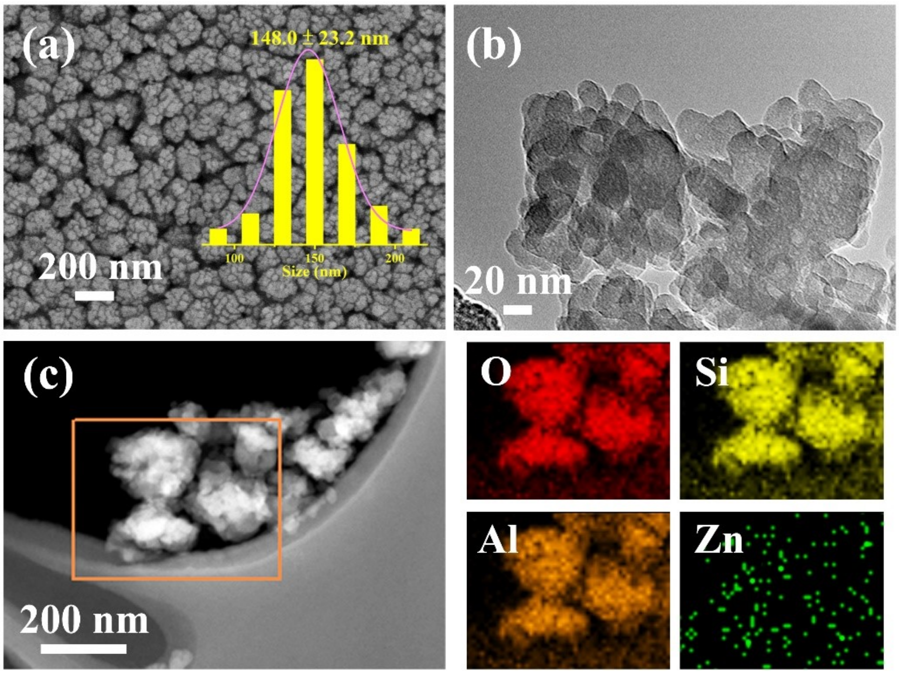

Fig. S3 (a) SEM images and particle size calculation of Zn/Z5, (b)TEM images of Zn/Z5, (c) TEM images and corresponding EDS elemental mapping of Zn/Z5.

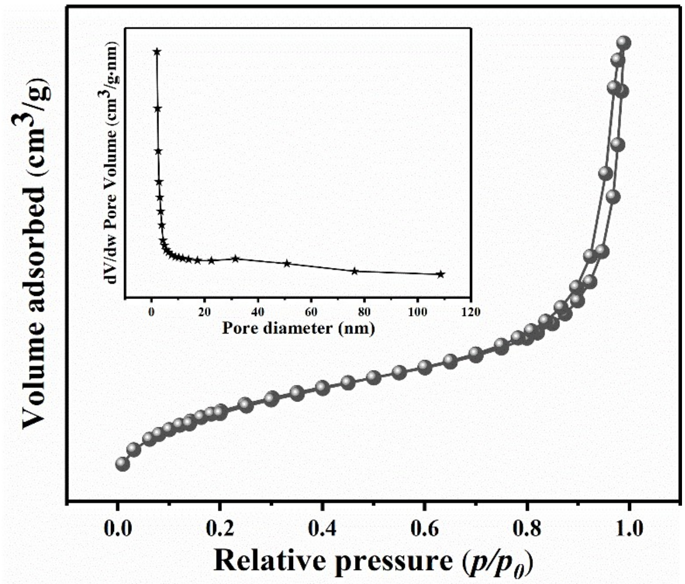

Fig. S4 N_2 adsorption-desorption isotherms and pore size distribution of Zn/Z5 zeolite.

Table S1. The textural properties of Zn/Z5 zeolite.

Samples	Zn (wt%)[a]	Suface area ($m^2 \cdot g^{-1}$)			Pore volume ($cm^3 \cdot g^{-1}$)		
		S_{BET}[b]	S_{micro}[c]	S_{meso}[d]	V_{total}[e]	V_{micro}[f]	V_{meso}[g]
Zn/Z5	0.93	431.15	268.99	162.16	0.40	0.12	0.28

[a] analysed by ICP-OES, [b] surface area determined by BET, [c] micropore surface area determined by t-plot, [d] $S_{meso} = S_{BET} - S_{micro}$, [e] total pore volume at $p/p_0 = 0.99$, [f] micropore volume determined by t-plot, [g] $V_{meso} = V_{BET} - V_{micro}$.

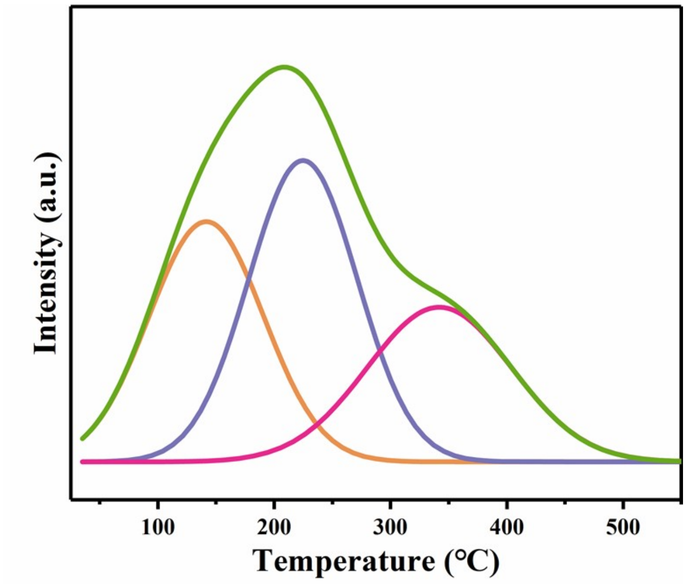

Fig. S5 NH_3-TPD profile of Zn/Z5 zeolite.

Table S2. Acidic properties of Zn/Z5 zeolite determined by NH_3-TPD.

Samples	The concentration of acid sites (a.u.·g^{-1})			
	Weak	Medium	Strong	Total
Zn/Z5	72.28	80.46	79.56	232.30

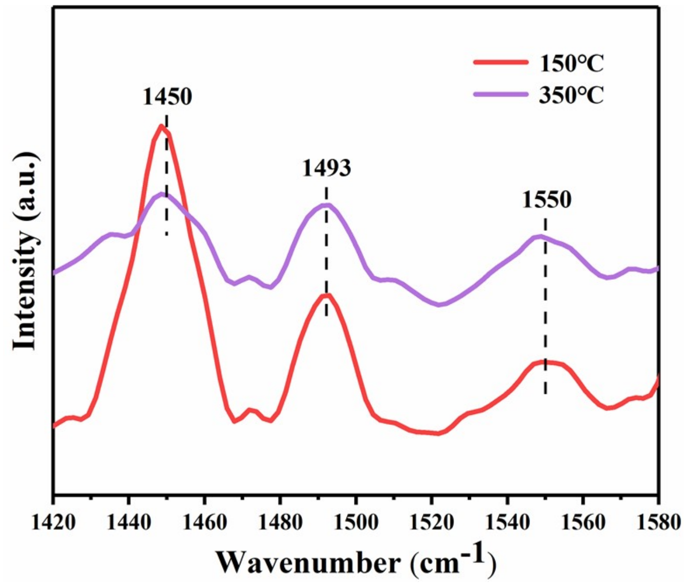

Fig. S6 Py-IR spectra of Zn/Z5 zeolite at 150°C and 350°C.

Table S3. Distribution of B and L acid sites on Zn/Z5 zeolite determined by Py-IR.

Samples	Amount of B ($mmol\cdot g^{-1}$)			Amount of L ($mmol\cdot g^{-1}$)		
	150°C	350°C	Total	150°C	350°C	Total
Zn/Z5	0.074	0.067	0.141	0.355	0.183	0.538

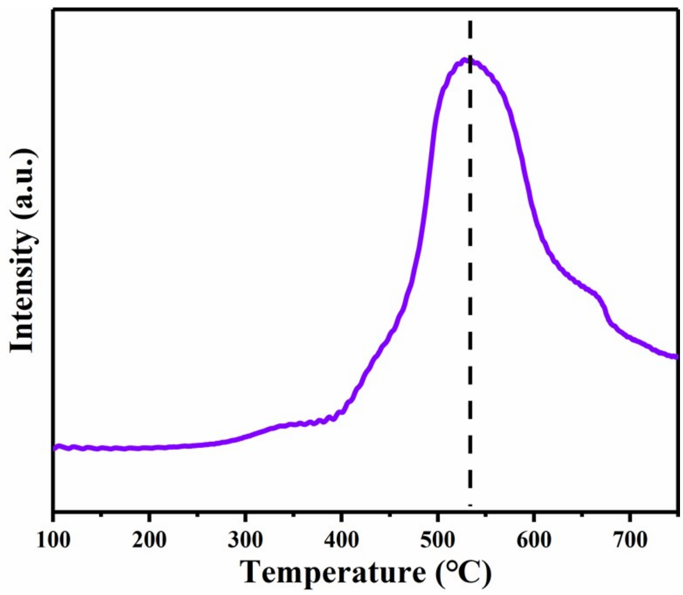

Fig. S7 H_2-TPR profile of Zn/Z5 zeolite.

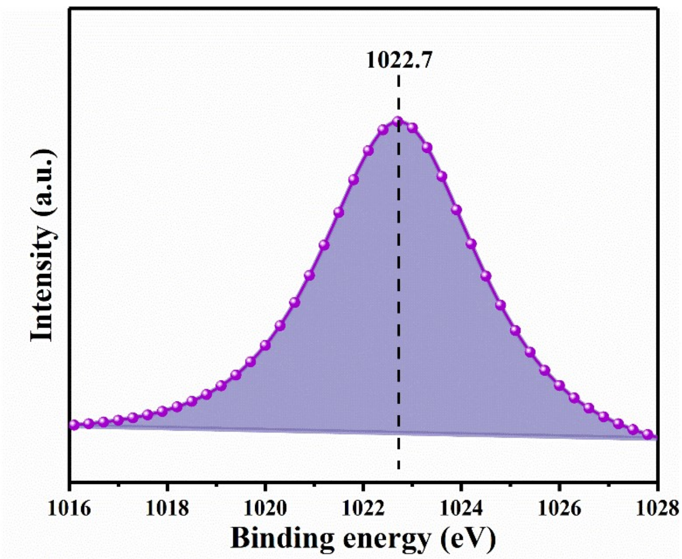

Fig. S8 XPS spectrum of Zn ($2p_{3/2}$) of Zn/Z5 zeolite.

The acidic properties of Zn/Z5 zeolite were studied by NH_3-TPD. As shown in Figure S5, three different NH_3 desorption peaks were detected in the low temperature zone (50-150°C), medium temperature zone (150-300°C) and high temperature zone (300-450°C). It shows that there are three types of acid centers in Zn/Z5 zeolite, corresponding to weak acid, medium strong acid and strong acid[1, 2]. The concentration of different acid sites was listed in Table S2. The concentration of weak acid sites, medium strong acid sites and strong acid sites of Zn/Z5 zeolite were 72.28, 80.46 and 79.56 a.u.·g^{-1}, respectively. The Brønsted (B) acid sites and Lewis (L) acid sites of Zn/Z5 zeolite at 150°C and 350°C were analyzed by Py-IR spectroscopy. As shown in Figure S6, three infrared absorption peaks were detected in Zn/Z5 zeolite. The absorption peak of pyridine molecules at 1450 cm^{-1} is attributed to L acid sites, the absorption peak of pyridine molecules at 1550 cm^{-1} is attributed to B acid sites and the absorption peak of pyridine molecules at 1493 cm^{-1} is attributed to the combined action of B acid sites and L acid sites[3, 4]. The detailed distribution results of B acid sites and L acid sites were listed in Table S3. The concentration of B acid sites and L acid sites of Zn/Z5 zeolite were 0.141 and 0.538 mmol·g^{-1}, respectively. In order to deeply study the interaction between Zn and Z5 zeolite in Zn/Z5 catalyst, the presence of Zn species in Zn/Z5 catalyst was analyzed by H_2-TPR and XPS, respectively. Figure S7 shows the H_2-TPR profile of Zn/Z5 zeolite. It can be found that a typical reduction peak appears at about 545°C, which is attributed to the $ZnOH^+$ species produced by the strong interaction between Zn and Z5 zeolite framework[5, 6]. This was also confirmed by the XPS spectrum of Zn $2p_{3/2}$ on the Zn/Z5 zeolite surface (Figure S8), and the energy spectrum peak attributed to the $ZnOH^+$ species at 1022.2 eV[7, 8].

Notes and references

1. Y. Bi, Y. Wang, X. Chen, Z. Yu and L. Xu, *Chin. J. Catal.*, 2014, **35**, 1740-1751.
2. X. Niu, J. Gao, Q. Miao, M. Dong, G. Wang, W. Fan, Z. Qin and J. Wang, *Micropor. Mesopor. Mater.*, 2014, **197**, 252-261.
3. K. Ji, J. Xun, P. Liu, Q. Song, J. Gao, K. Zhang and J. Li, *Chin. J. Chem. Eng.*, 2018, **26**, 1949-1953.
4. A. S. Al-Dughaither and H. de Lasa, *Ind. Eng. Chem. Res.*, 2014, **53**, 15303-15316.
5. X. Su, K. Zhang, Y. Snatenkova, Z. Matieva, X. Bai, N. Kolesnichenko and W. Wu, *Fuel Process. Technol.*, 2020, **198**.
6. X. Su, W. Zan, X. Bai, G. Wang and W. Wu, *Catal. Sci. Technol.*, 2017, **7**, 1943-1952.
7. X. Niu, J. Gao, K. Wang, Q. Miao, M. Dong, G. Wang, W. Fan, Z. Qin and J. Wang, *Fuel Process. Technol.*, 2017, **157**, 99-107.
8. J. Chen, L. Chang, H. Kang and F. Ding, *Chin. J. Catal.*, 2001, **22**, 229-232.