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Ethane aromatization and evolution of carbon deposits over nanosized and microsized Zn/ZSM-5 catalysts

Yan Zhang, [a] *Shide Wu,* [b] *Xia Xu* [a, c] *and Heqing Jiang* * [a, c]

[a]Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. E-mail: jianghq@qibebt.ac.cn; Tel.: +86 532 80662716; Fax: +86 532 80662716

[b]Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450001, China

[c]University of Chinese Academy of Sciences, Beijing 100049, China

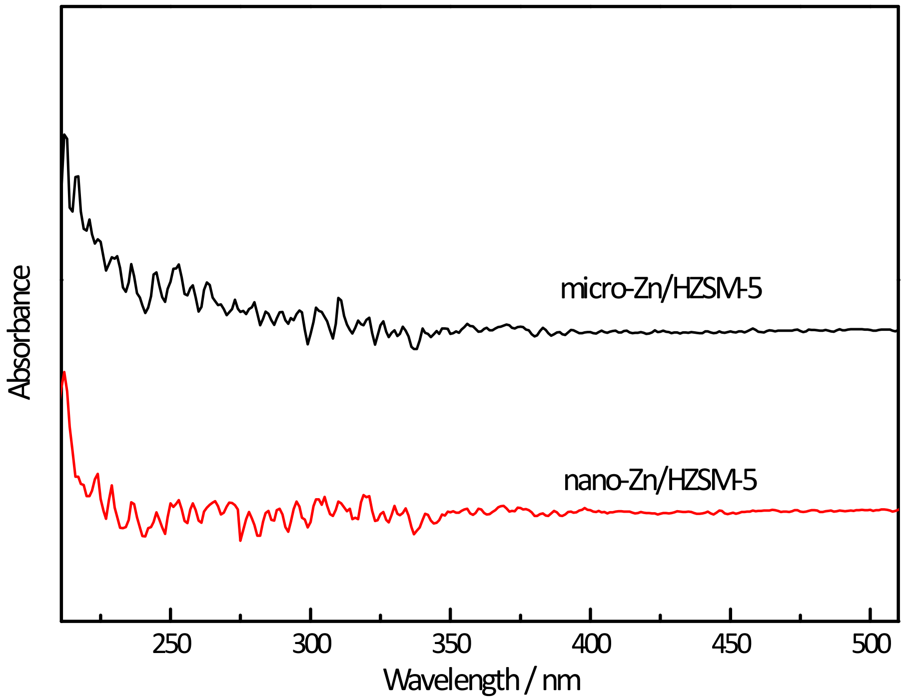

Fig. S1 UV-vis diffuse reflectance spectra for micro-Zn/HZSM-5 and nano-Zn/HZSM-5.

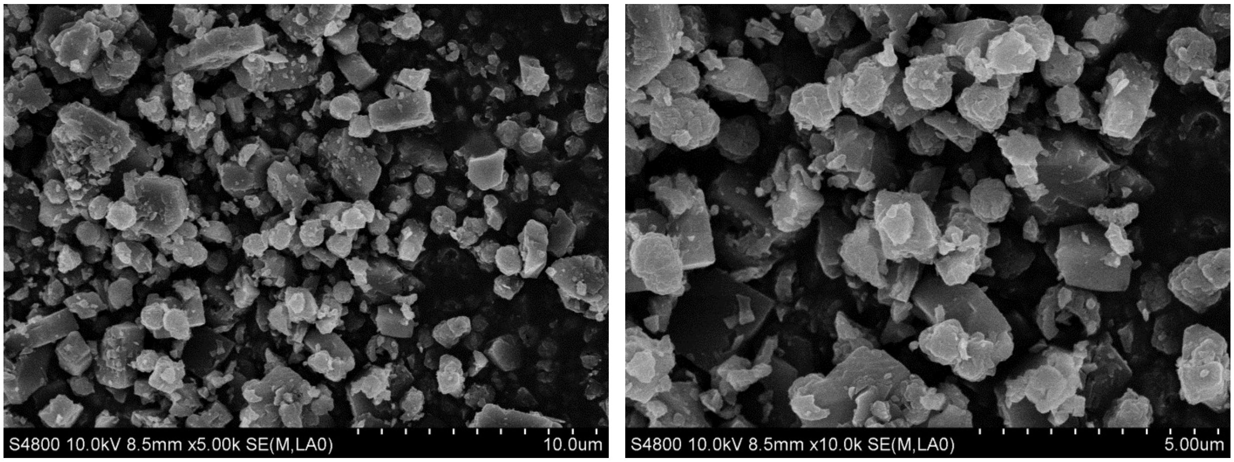

Fig. S2 SEM images of micro-Zn/HZSM-5.

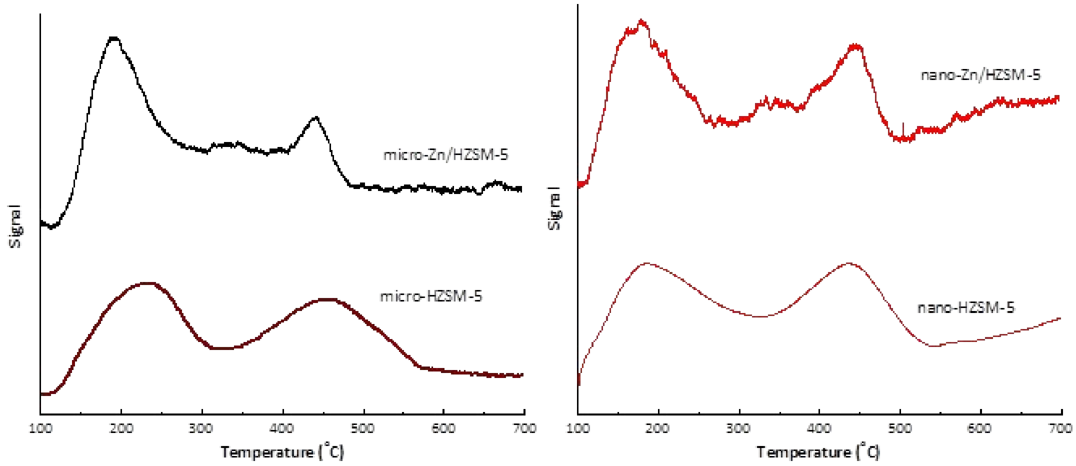

Fig. S3 NH_3-TPD profiles of HZSM-5 and Zn/HZSM-5 samples.

Typicallly, TPD patterns suggested that the Zn dispersions of the micro-Zn/HZSM-5 and nano-Zn/HZSM-5 catalysts might be comparable. The evidence came from the observation that these catalysts exhibit similar NH_3 desorption patterns including the low-temperature and high-temperature NH_3 desorption peaks. The high temperature NH_3 desorption is generally related to those ammonia molecules adsorbed on the zeolite's Brønsted acid sites and the reduction of its intensity is often used to evaluate the catalyst's Zn dispersion.[1,2] Namely, weakened intensity of the strong high temperature NH_3 desorption from the NH_3-TPD patterns suggests that part of Brønsted acid sites in the zeolites of these catalysts were occupied by Zn species, which is essential for the title catalytic reaction. According to Wu et al.[3] and Xu et al.,[4] these variations can further prove that the incorporated Zn species reacted with the Brønsted acid sites of the ZSM-5 zeolite and thus formed the $ZnOH^+$ species, which was unstable and further reacted to form the binuclear $[ZnOZn]^{2+}$ species that act as the Lewis acid sites.

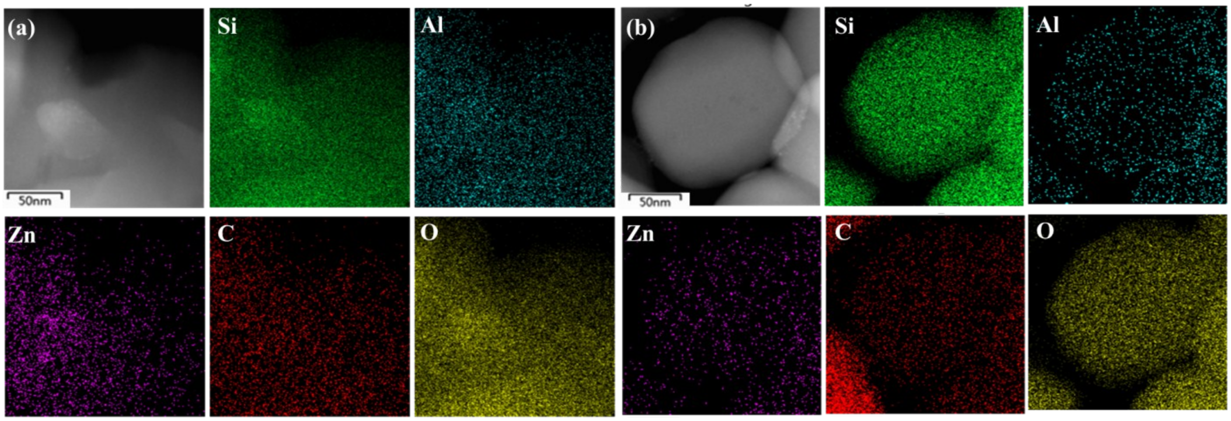

Fig. S4 STEM-EDS elemental maps of the spent (a) micro-Zn/HZSM-5 and (b) nano-Zn/HZSM-5 catalysts after ethane aromatization reaction (1000 min in continuous ethane flow at 575 ^{o}C) .

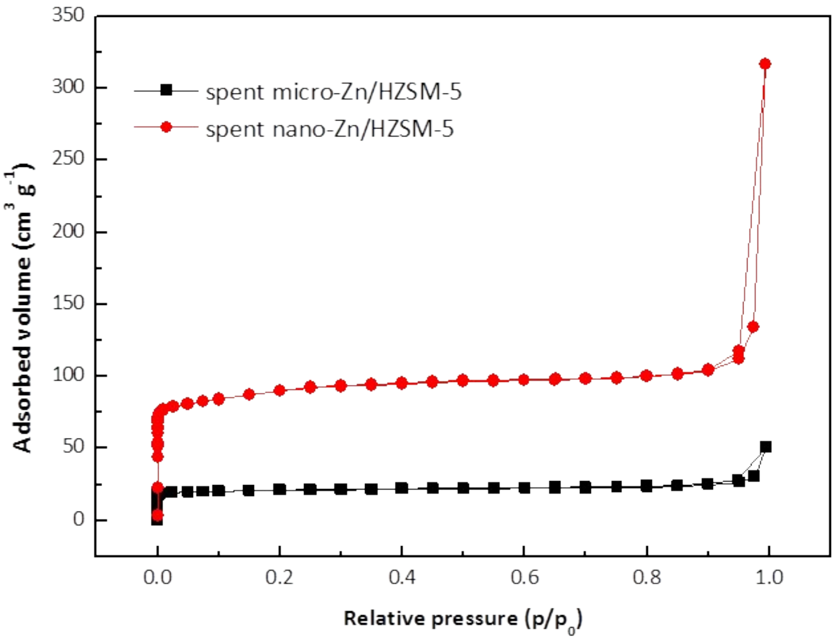

Fig. S5 N_2 adsorption-desorption isotherms of spent micro-Zn/HZSM-5 and nano-Zn/HZSM-5 samples (1000 min in continuous ethane flow at 575 ^{o}C).

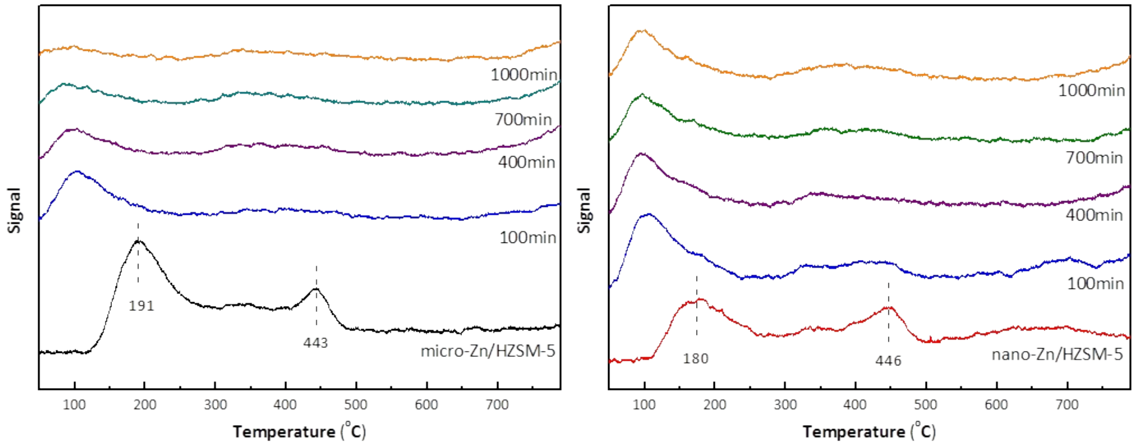

Fig. S6 Ammonia temperature programmed desorption (NH_3-TPD) profiles of micro-Zn/HZSM-5 and nano-Zn/HZSM-5 samples exposed to ethane at 575 ^{o}C for different times.

The changes of acidic properties of the catalysts with time-on-stream were studied by NH_3-TPD experiments. As shown in Figure S6, typically, besides the observed peak in the region of 300-400 ^{o}C that can be assigned to medium acidic sites, the spectra of micro-Zn/HZSM-5 and nano-Zn/HZSM-5 samples exhibit two characteristic peaks in the low-temperature region of 180-191 ^{o}C and the high-temperature region of 443-445 ^{o}C, which were attributed to the adsorbed NH_3 on weak and strong acid sites, respectively.[5,6] However, there were obvious shifts towards lower temperatures for both of the micro- and nano-sized catalysts with time-on-stream, indicating that the strength of the acid sites of the zeolite catalysts became weaker after treatment under standard reaction conditions (10 % C_2H_6, 575 ^{o}C). Moreover, as the time on stream was prolonged, first the intensity of the peak for strong acid sites clearly reduced and then for the weak acid sites, as shown in Figure S6. These changes indicated that the accumulated coke blocked the zeolite acidic sites and the active metal centers, thus leading to the inevitable decline in catalytic performance as displayed in Figure 8 in the manuscript. It is noteworthy that, compared with the abruptly decreased intensity of acidic peaks over micro-

Zn/HZSM-5, obvious maintaining of acidic properties was observed for nano-Zn/HZSM-5 with time-on-stream, implying the suppression of coke accumulation during reaction for nanosized catalysts.

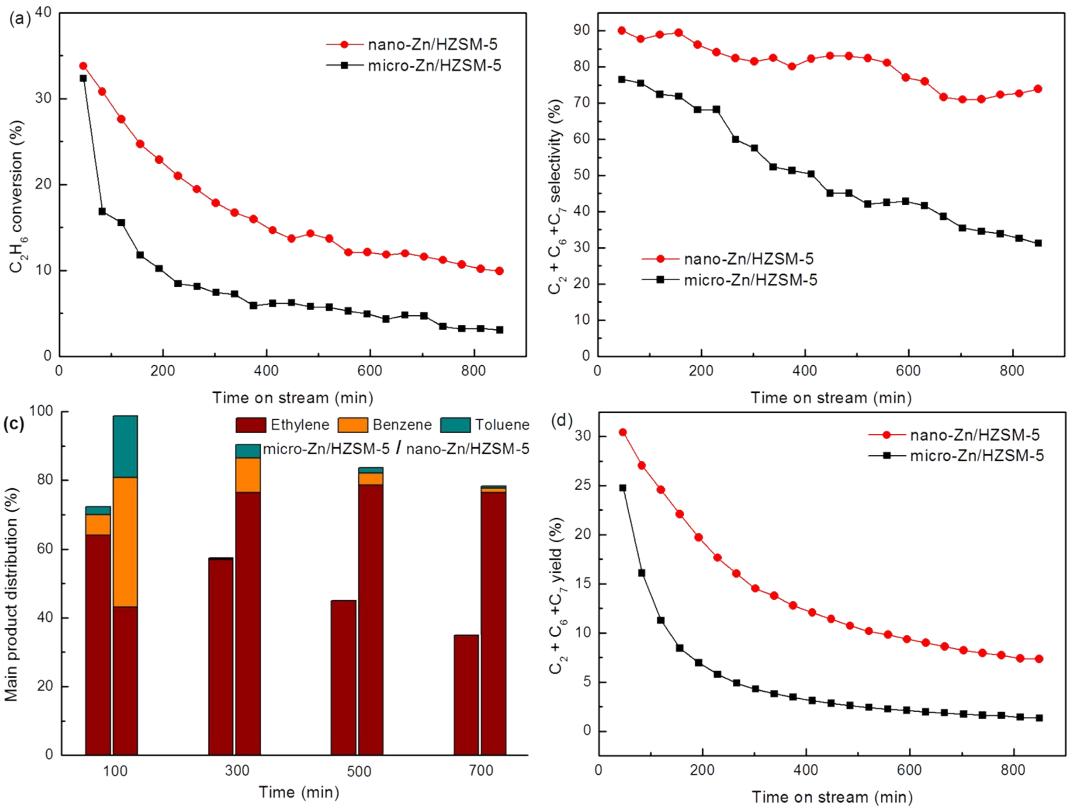

Fig. S7 (a) Conversion of C_2H_6, (b) selectivity of ethylene and aromatics (benzene and toluene), (c) corresponding product distribution and (d) yield of products as a function of time during ethane aromatization. Catalyst weight: 0.2 g. Flow rate: 15 mL min^{-1} (30 vol% C_2H_6 + 5 vol% N_2 + 65 vol% He).

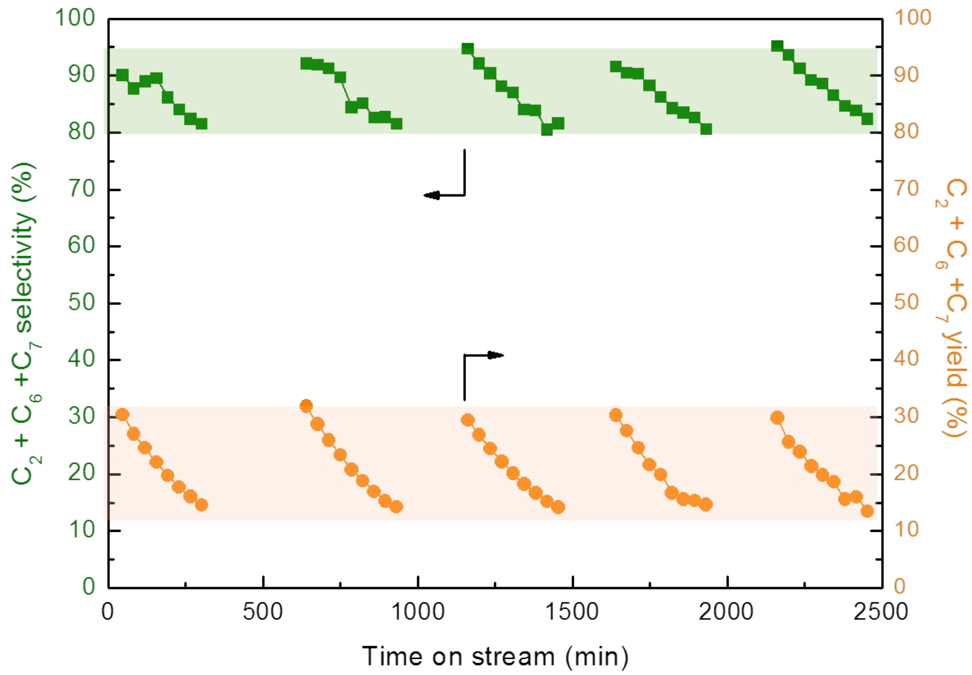

Fig. S8 Selectivity and yield of ethylene and aromatics (benzene and toluene) of nano-Zn/HZSM-5 as a function of time during ethane aromatization with periodic regeneration. Catalyst weight: 0.2 g. Reaction conditions: Flow rate = 15 mL min^{-1} (30 vol% C_2H_6 + 5 vol% N_2 + 65 vol% He), T = 575 ^{o}C. Regeneration conditions: air, flow rate = 15 mL min^{-1}, T = 575 ^{o}C.

Table S1 Textural properties of the fresh and spent micro-Zn/HZSM-5 and nano-Zn/HZSM-5 samples.

Sample	S_{BET}[a] (m^2 g^{-1})	S_{Micro}[b] (m^2 g^{-1})	$S_{External}$[b] (m^2 g^{-1})	V_{Total}[c] (cm^3 g^{-1})	V_{Micro}[b] (cm^3 g^{-1})	V_{Meso}[d] (cm^3 g^{-1})
fresh micro-Zn/HZSM-5	272	253	19	0.135	0.106	0.029
spent micro-Zn/HZSM-5	83	78	4	0.078	0.031	0.047
fresh nano-Zn/HZSM-5	327	278	49	0.223	0.124	0.099
spent nano-Zn/HZSM-5	316	298	18	0.207	0.137	0.070

[a] Determined by BET method

[b] Determined by t-plot method

[c] Determined at $p/p_0 = 0.974$

[d] $V_{Meso} = V_{Total} - V_{Micro}$

Notes and references

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