Function of well-established mesoporous layers of recrystallized ZSM-22 zeolites on the catalytic performance of n-alkanes isomerization

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1. Characterizations

X-ray diffraction (XRD) was applied to distinguish the phases of different samples, which was recorded on a Bruker D8 Advance with Cu Ka (γ = 1.5418 Å) radiation operating at 40 kV and 40 mA at a stepwise increase of 0.02º in the 2θ range from 1º to 50°.

N_2 adsorption-desorption was performed at -196 ℃ on a Micromeritics ASAP 2020 analyzer. The specific surface areas of different samples were calculated with Brunauer-Emmett-Teller (BET) method. Prior to measurements, the samples were degassed at 350 ℃ for 8 h under vacuum.

The inductively coupled plasma (ICP) analysis was carried out on a PerkinElmer Optima 2100DV to determine the bulk chemical composition. The surface Si and Al contents were investigated by X-ray photoelectron spectroscopy (XPS) on a Physical Electronics Company Quantum-2000 scanning ESCA microprobe with Al Kα radiation. The XPS signal were conducted using Gaussian/Lorentzian (70/30) product function. Molar fractions of Si and Al were calculated using the sensitivity factors (Si_{sf} = 0.82, Al_{sf} = 0.54) provided by manufacturer and the transmission function.

Transmission electron microscope (TEM) images were recorded on FEI Tecnai G2 F30 operating at 300 kV for high resolution measurements. Before the measurement, the catalysts were reduced in H_2 flow (50 mL/min) at 400 °C for 2 h.

Fourier transform infrared spectroscopy with pyridine or 2,6-dimethylpyridine adsorption (Py- and DM-IR) analysis was performed by a Bruker FT-IR spectrometer to determine the acid types of different samples. Before the measurement, the sample about 15 mg was pressed and placed in the FTIR cell. The latter was evacuated under vacuum at 400 °C for 60 min. After decreasing to 30 °C, the background spectrum of the sample was recorded. Pyridine or 2,6-dimethylpyridine was absorbed on the sample

for 30 min followed by desorption at 200 °C and 350 °C for 60 min to remove the physiosorbed pyridine, and the IR spectra were respectively recorded in the range of 1400-1580 cm^{-1} and 1550-1700 cm^{-1}. The quantitative calculation of B acidity is based on the Lambert-Beer Law [1] for Py-IR and DMPy-IR. According to the reported literatures [2,3], the molar extinction coefficients for Py-IR and DMPy-IR are is used for the calculations.

CO pulse chemisorption experiment was used to study the Pt dispersion (D_{Pt}) and particle sizes, and performed on Micromeritics ASAP 2920 apparatus with a TCD detector. Prior to analysis, the bifunctional catalyst (200 mg) was in-situ reduced in H_2 flow (50 mL/min) at 400 °C for 120 min, followed by flushing with He (50 mL/min) at 450 °C for 30 min. After cooling down to 50 °C, several pluses of adsorption gas (5% CO in helium) were injected at constant intervals until saturation with CO molecule. The Pt dispersion and particle size were calculated assuming the stoichiometry of CO/Pt = 1.

2. Results
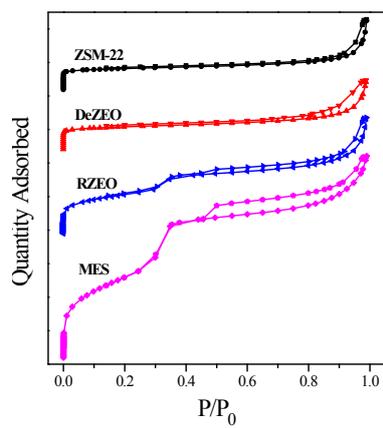
Fig. S1 N_2-adsorption isotherms of original ZSM-22, DeZEO, RZEO and MES materials
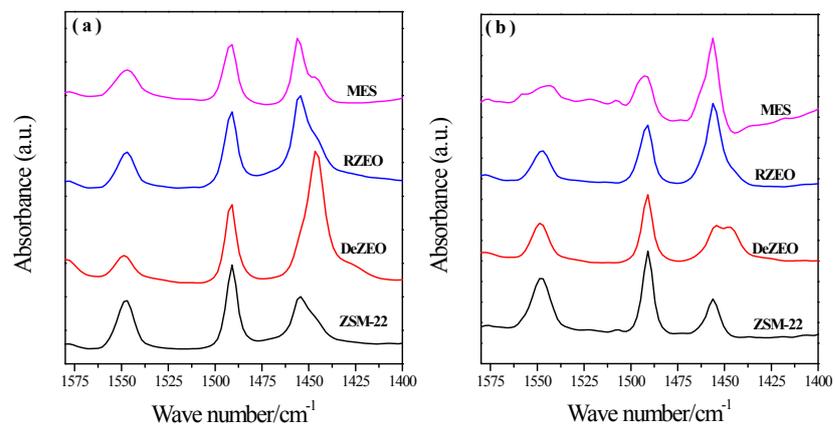
Fig. S2 Pyridine adsorbed FT-IR spectra of various materials at 200 °C (a) and 350 °C (b).
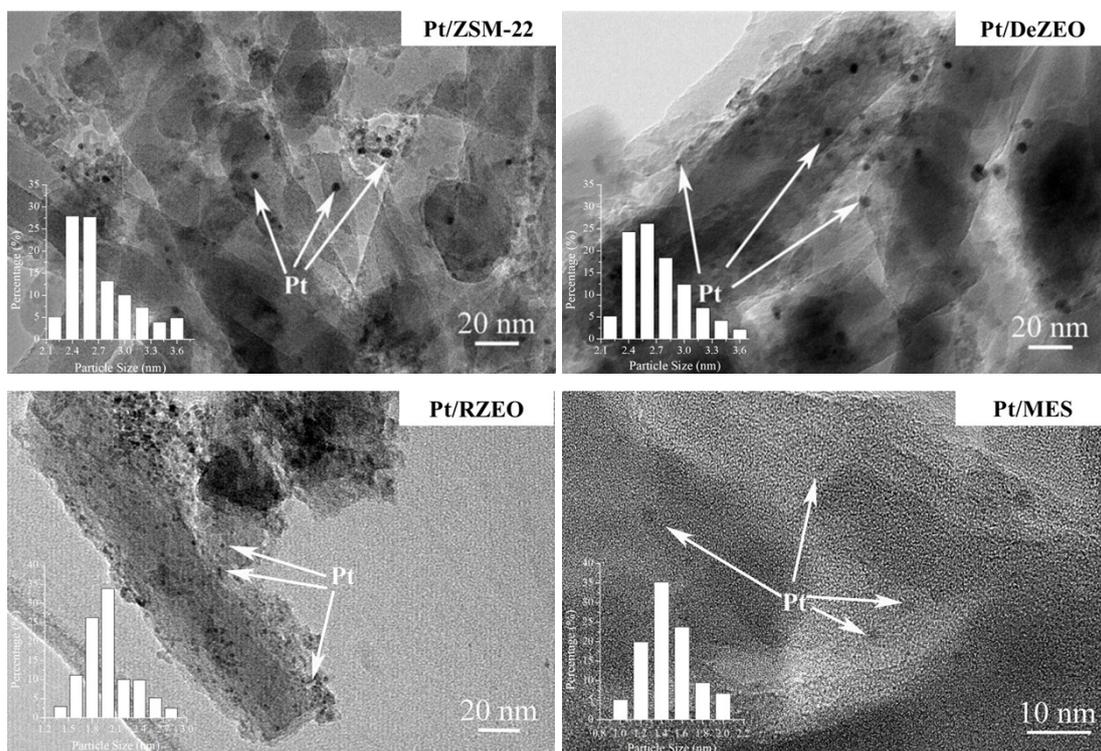
Fig. S3 TEM images and particle size distribution of different catalysts reduced at 400 °C.

Table S1 Summary of the catalytic performance of ZSM-22 zeolites for n-alkane isomerization in the literatures and present work.

Catalysts	Isomerization performance	Reaction Conditions	Ref.
Pt/ZSM-22 [1]	Con.=80.0 %, Sele. =93.7 %	5.0 MPa, 300 °C	[4]
hierarchical Pt/ZSM-22 [2]	Con. = 89 %, Sele. = 92.1%	0.45 MPa; 1400 kg s mol^{-1}.	[5]
Pt/Ba-H-ZSM-22 [3]	Con.=89.9%, Sele. =85.8 %	60 kPa, 1.1 h^{-1}, 310 °C	[6]
Pt/ZAT-0.07	Con.=80.0%, Sele. =87.3 %	2.0 MPa, 2.0 h^{-1}, 280 °C	[7]
Pt/ZSM-22-(NH$_4$)$_2$SiF$_6$	Con.=87.5%, Sele. =88.2 %	6.0 MPa, 1.04 h^{-1}, 300 °C	[8]
Pt/H-[Al,Fe]-ZSM-22	Con.=90.6%, Sele. =87.0 %	2.0 MPa, 2.0 h^{-1}, 330 °C	[9]
Pt/ H-[Al,Ga]-ZSM-22	Con.=90.4%, Sele. =78.19%	2.0 MPa, 2.0 h^{-1}, 320 °C	[10]
Pt/B-ZSM-22	Con.=82%, Sele. = 89%	4.0 MPa, 1.2 h^{-1}	[11]
Pt/RZEO [4]	Con.=91.3%, Sele. = 91.7%	2.0 MPa, 2.0 h^{-1}, 320 °C	Present work

1, n-C$_8$ as reactant; 2, n-C$_{10}$ as reactant; 3, n-C$_{16}$ as reactant; 4, n-C12 as reactant.

References

[1] L. Guo, X. Bao, Y. Fan, G. Shi, H. Liu, D. Bai, J. Catal., 2012, 294, 161.

[2] S. Zeng, J. Blanchard, M. Breysse, Y. Shi, X. Shu, H. Nie, D. Li, Micro. Meso. Mater., 2005, 85, 297.

[3] T. Onfroy, G. Clet, M. Houalla, Micro. Meso. Mater., 2005, 82, 99.

[4] D. Verboekend, K. Thomas, M. Milina, S. Mitchell, J. Pérez-Ramírez, J.-P. Gilson, Catal. Sci. Technol., 2011, 1, 1331.

[5] J. A. Martens, D. Verboekend, K. Thomas, G. Vanbutsele, J. Pérez-Ramírez, J.-P. Gilson, Catal. Today, 2013, 218-219, 135.

[6] S. Parmar, K. K. Pant. M. John, K. Kumar, S. M. Pai, B. L. Newalkar, J. Mol. Catal. A: Chem., 2015, 404, 47.

[7] X, Wu, M. Qiu, X. Chen, G. Yu, X. Yu, C. Yang, J. Sun, Z. Liu, Y. Sun, New J. Chem., 2018, 42, 111.

[8] G. Wang, Q. Liu, W. Su, X, Li, Z. Jiang, X. Fang, C. Han, C. Li, Appl. Catal. A: Gen., 2008, 335, 20

[9] S. Liu, J. Ren, S. Zhu, H. Zhang, E. Lv, J. Xu, Y.-W. Li, J. Catal., 2015, 330, 485.

[10] S. Liu, Y. He, H. Zhang, Z. Chen, E. Lv, J. Ren, Y. Yun, X. Wen, Y.-W. Li, Catal. Sci. Technol., 2019, 9, 2812.

[11] P. Niu, P. Liu, H. Xia, J. Ren, M. Lin, Q. Wang, X. Chen, L. Jia, B. Hou, D. Li, Appl. Catal. A, Gen., 2018, 562, 310.