

Supporting Information

Mo-modified ZSM-5 zeolite with intergrowth crystals for high-efficiency catalytic
xylene isomerization

Lei Miao, Zhe Hong, Guoqing Zhao, Fangtao Huang, Zhirong Zhu*

School of Chemical Science and Engineering, Tongji University, Shanghai 200092, P.
R. China

* To whom correspondence should be addressed.

E-mail: zhuzhirong@tongji.edu.cn

Tel: (+86) 021-65982836

Catalyst preparation

All the agents were of analytical grade and were used without further purification. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (shanghai, China).

1.1 Synthesis of ZSM-5 with symbiotic crystal structure

In a typical synthesis, NaAlO₂, TPAOH and NaOH were dissolved in distilled water (solution A). Solutions A and B (tetraethyl orthosilicate) were slowly added into the three-necked flask at room temperature with vigorous stirring. The solution was further stirred for 3 h. The molar ratio of the obtained precursor mixture solution was 76 SiO₂:1 Al₂O₃:2 TPAOH:1.83 Na₂O: 360 H₂O. The mixture was stirred at room temperature for 4 h. Heated in a Teflon autoclave at 393 K for two hours, then heated to 443 K for 72 hours. After cooling to room temperature, the obtained product was washed with distilled water until the pH was neutral. Then, the samples were dried at 120°C for 12 hours and calcined at 550°C for 6 hours.

1.2 Coffin shape ZSM-5 preparation

Na-form ZSM-5 with a Si/Al ratio of 38 was prepared by a traditional hydrothermal method according to the reported procedure^{1,2}.

1.3 Preparation of Mo/ZSM-5 catalysts

Exchange Na-ZSM-5 and C-ZSM-5 with 1mol/L NH₄Cl solution (solid/liquid ratio, 1 g/4 mL) at 95°C for 4 h, then filter and wash with distilled water. The sample was dried at 120°C for 12 h. The NH₄Cl aqueous solution ion-exchange process was

repeated three times. The ZSM-5 was vacuum immersed in the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ solution for metal loading modification. The samples were calcined at 520°C for two hours, and the heating rate was $3^\circ\text{C}/\text{min}$. All these prepared catalyst samples were reduced in a hydrogen stream at 380°C for 2 h. Finally, the xylene isomerization catalysts $x\text{Mo}/\text{ZSM-5}$ were obtained, where x was the content of Mo.

Catalyst characterizations

The elemental compositions in the resultant catalyst was determined by inductively coupled plasma optical emission spectroscopy (Agilent ICP-725ES, Agilent Technologies, USA). The structure of the catalysts was determined by X-ray diffraction (XRD) technology on a Bruker AXS-D8 Advance Diffractometer with monochromatic Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) radiation at voltage and current of 40 kV and 40 mA. The specific surface area was measured by a Micromeritics ASAP 2460 Surface Area instrument by physisorption of nitrogen at -196°C . The samples were dehydrated at 300°C using vacuum degassing for 12 h before experiments. The specific surface area was calculated by the BET (Brunauer-Emmett-Teller) method.

The crystal morphology of ZSM-5 zeolite was observed by means of a scanning electron microscope (SEM, S-4800, Hitachi). NH_3 -TPD experiment was performed on a conventional set-up equipped with a TCD (CHEMBET 3000). The strength and number of the acidic sites was determined according to the temperature and the area of NH_3 desorption peaks. Infrared spectroscopy with pyridine adsorption (Py-IR) was obtained respectively at 473 K and 673 K, with Perkin-Elmer 2000 FT-IR spectrometry and a self-supported wafer of sample. Thermo gravimetric analysis (TGA) of the spent

catalyst was carried out on a METTLER TGA/DSC1/1600HT apparatus in air atmosphere at a heating rate of 10°C/min. According to the reported procedure, a mixture of n-hexane and 3-methylpentane is used to determine the constraint index of the zeolite³⁻⁵.

Catalytic reaction.

The xylene isomerization performance of the prepared catalysts were tested in a fixed-bed reactor equipped with a cooling system. The xylene mixture containing 62.5% MX, 30.2% OX and 7.3% EB was applied as a feed mixture. The catalyst (5 g) was filled in the reactor (1.5 cm inner diameter) and this reactor was sealed and heated to the designed reaction temperature. Before the reaction, the catalyst is activated in situ in a pure H₂ flow at 673 K for 1 h. Then, a liquid mixture xylene was introduced into the reactor with a volume flow of 0.38 mL/min. During the reaction, the products were analysed by GC, HP5890 equipped with a PEG-20M capillary column. The conversion of EB and Xylene loss rate were calculated as following.

$$\text{Conversion (\%)} = \left(1 - \frac{\text{The product of EB}}{\text{The feed of EB}} \right) \times 100\%$$

$$\text{Xylene loss (\%)} = \left(1 - \frac{\text{The produce of xylene}}{\text{The feed of xylene}} \right) \times 100\%$$

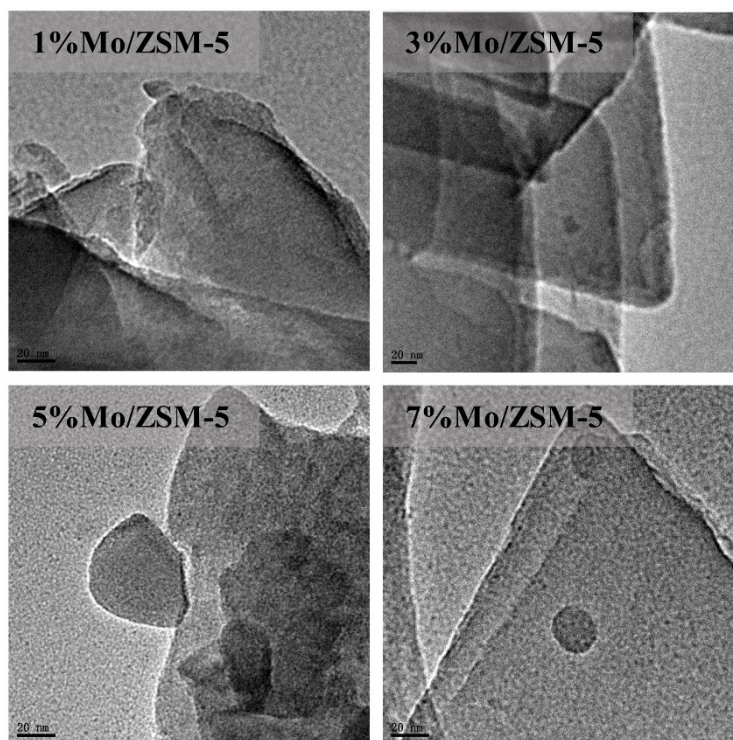


Figure S 1- TEM images of samples with different Mo content

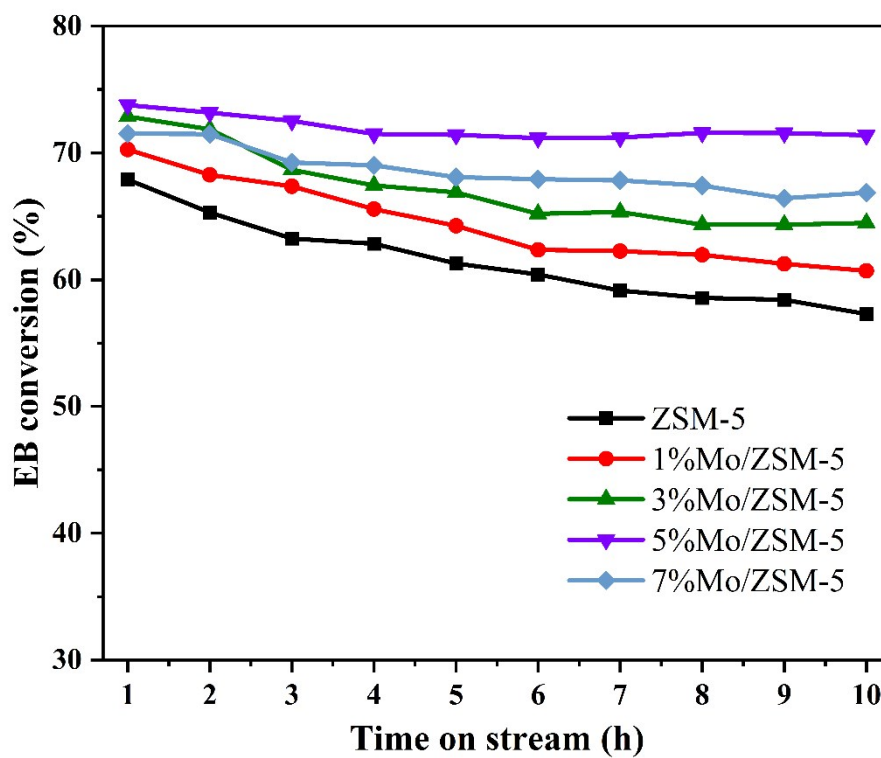


Figure S 2- The conversion of EB versus reaction time in the xylene isomerisation of C8 on Mo/ZSM-5 catalysts.

reaction conditions: $T = 380^{\circ}\text{C}$, $\text{WHSV} = 4.0 \text{ h}^{-1}$, $n(\text{H}_2)/n(\text{C}_8) = 4$, $P = 1.5 \text{ MPa}$.

References

1. C. Kongmanklang and K. Rangriwatananon, *J. Spectrosc.*, 2015, **2015**, 1-5.
2. M. Zhou and J. Hedlund, *RSC Adv.*, 2013, **3**, 15596.
3. Z. Zhu, Q. Chen, Z. Xie, W. Yang, D. Kong and C. Li, *J. Mol. Catal. A: Chem.*, 2006, **248**, 152-158.
4. Z. Hong, G. Zhao, C. Xiong, W. Jia, F. Huang and Z. Zhu, *Appl. Catal., A*, 2021, **612**, 117983.
5. R. Kumar and P. Ratnasamy, *J. Catal.*, 1989, **116**, 440–448.