

Electronic Supplementary Materials

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Modification of acidity in HZSM-5 zeolite for methane-methanol co-reaction

Bing-jie ZHOU¹, Zhi-xiang XI¹, Yue YU¹, Bin-bo JIANG^{†1}, Jing-dai WANG^{1,2},
Zu-wei LIAO¹, Zheng-liang HUANG¹, Yong-rong YANG^{1,2}

¹*Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology,
Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China*

²*State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*

[†]E-mail: jiangbb@zju.edu.cn

Captions

Table S1 Comparison of methane dehydro-aromatization reactions and co-reaction of methane and methanol

Table S2 Catalytic performance of methane and methanol co-reaction

Fig. S1 Infrared spectra of catalyst C-3

Table S1 Comparison of methane dehydro-aromatization reactions and co-reaction of methane and methanol

Catalyst	Reaction temperature (K)	Methane conversion (%)	Reference
Nanoscale Mo/HZSM-5	973	10.5	Wang et al., 2004
Mo/HZSM-5	973	6.0	Liu H et al., 2011
Zn/ZSM-5	973	5.5	Liu BS et al., 2011
GaZn/ZSM-5	973	7.4	Liu BS et al., 2011
ZSM-5	673	5.4	Our work

Liu BS, Zhang Y, Liu JF, et al., 2011. Characteristic and mechanism of methane dehydroaromatization over Zn-based/HZSM-5 catalysts under conditions of atmospheric pressure and supersonic jet expansion. *The Journal of Physical Chemistry C*, 115(34):16954-16962. <https://doi.org/10.1021/jp2027065>

Liu H, Wu S, Guo Y, et al., 2011. Synthesis of Mo/IM-5 catalyst and its catalytic behavior in methane non-oxidative aromatization. 90(4):1515-1521. <https://doi.org/10.1016/j.fuel.2010.11.027>

Wang DY, Kan QB, Xu N, et al., 2004. Study on methane aromatization over MoO₃/HMCM-49 catalyst. *Catalysis Today*, 93-95:75-80. <https://doi.org/10.1016/j.cattod.2004.05.015>

Table S2 Catalytic performance of methane and methanol co-reaction

Entry	Catalyst	Conversion (%)		Selectivity (%)				
		Methane	Methanol ^{***}	C ₂ +C ₃	C ₂ ⁼ +C ₃ ⁼	C ₄	C ₅ ⁺	BTX
1	C-0	4.06	100	23.09	4.55	24.24	15.58	32.54
2	Al ₂ O ₃ [*]	0	0.13	39.37	26.42	0	34.20	0
3	Mixture ^{**}	3.91	100	21.67	5.49	24.77	16.97	31.09

Reaction conditions: for entry 1&2, 0.96 g sample, $T=673$ K, $WHSV_{CH_3OH}=2$ h⁻¹, $P_{CH_3OH}=30$ kPa, $P_{CH_4}=30$ kPa; for entry 3, 1.056 g sample, $T=673$ K, $WHSV_{CH_3OH}=2$ h⁻¹, $P_{CH_3OH}=30$ kPa, $P_{CH_4}=30$ kPa.

^{*} Aluminum oxide was synthesized through a mixture of NaAlO₂ solution and HCl solution. The precipitate was filtered, then washed with deionized water and dried at 110 °C. Finally, the sample was calcined in air at 550 °C for 4 h.

^{**} 90.9% ZSM-5 and 9.1% aluminum oxide were mixed and well grinded, then the sample was tableted under 30 kg pressure, crushed and sieved into 20-40 mesh.

^{***} Take both methanol and dimethyl-ether as reactants.

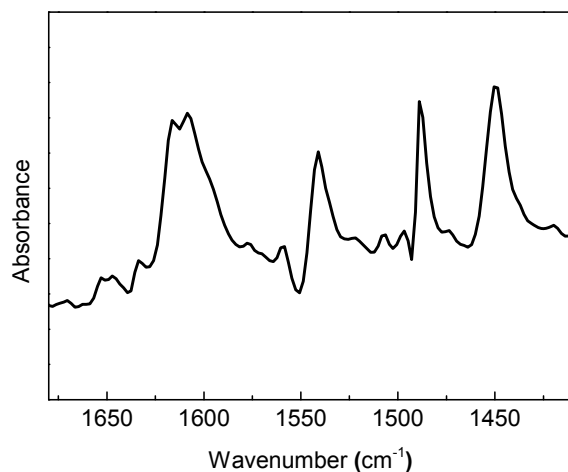


Fig. S1 Infrared spectra of catalyst C-3

The acidic property of C-3 was studied by adsorption and temperature programmed desorption (TPD) of pyridine by Fourier transform infrared (FT-IR) spectroscopy. The infrared spectra were recorded on a Bruker tensor 27. About 40 mg self-supporting wafer (diameter 2 cm) of the sample was evacuated in a home-made vacuum infrared cell having KBr windows. The material was dried at 430 °C for 2 h under vacuum. After cooling down, the sample reference spectra were recorded at 50 °C. The the evacuated sample was saturated with pyridine vapor at 150 °C for 1 min (two times). The saturated sample was evacuated at 150 °C for 1 h. Then the sample was cooled down to 50 °C and infrared spectra of adsorbed pyridine was recorded.