Electronic supplementary information (ESI)

Reaction mechanism for the conversion of methanol to olefins over H-ITQ-13 zeolite: a density functional theory study

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As the Electronic supplementary information (ESI) of the manuscript "*Reaction* mechanism for the conversion of methanol to olefins over H-ITQ-13 zeolite: a density functional theory study", supplementary data and related discussion are provided.

1. About the 79T cluster model and location of Ge and Al in H-ITQ-13

A 79T cluster model was built, including three characteristic channels (10-MR sinusoidal, 10-MR straight, and 9-MR straight) and their intersection region, which serves as the main catalytic center for the MTO reactions.^{1,2} In this model, one Ge atom is located at T2 site and one Al atom at T3 site; the charge-balancing protons are produced at O8 or O9.

To determine the definite location of Ge in the strained double four rings (D4R), the relative substitution energies are calculated by substituting Si with Ge at each site in D4R (T2-1, T2-2, T2-3, T2-4, T5-1, T5-2, T5-3, and T5-4, as shown in Fig. S-1); the relative substitution energies are determined by taking the substitution with the lowest free energy as the reference state. The calculated relative substitution energies, as given in Table S1, suggest that the formation of Ge-O-Al is favorable and such a cluster model is quite reasonable.

The content of Ge in this model is somewhat lower than the optimal value reported by Li and co-workers.³ However, another cluster model of 79T including two Ge atoms, which had a Si/Ge atomic ratio of 39.5 was also considered, with Al atoms located at the same position. As given in Table S2, two models with different Ge contents lead to the similar calculation results, since the MTO reaction behavior is mainly determined by the location of Al atoms that make for the acid sites active for MTO.



Fig. S1 Double four rings in the 79T cluster model with eight T sites named as T2-1, T2-2, T2-3, T2-4, T5-1, T5-2, T5-3, and T5-4.

Ge site	RSE (kJ mol ⁻¹)
T2-1	0
T2-2	46
T2-3	56
T2-4	19
T5-1	11
T5-2	42
T5-3	42
T5-4	22

Table S1 Calculated relative substitution energies (RSE) of germanium in the [Ge]-ITQ-13

 zeolite

Table S2 Calculated intrinsic free energy barriers (ΔG_{int}^{\neq}) of the gem-methylation reaction 2MB \rightarrow 3MB⁺ on the H-ITQ-13 cluster model with two germanium atoms, in comparison with the model used in this work with one germanium atom

model	$\Delta G_{\rm int}^{\neq}$ (kJ mol ⁻¹)
one Ge atom: Ge(T2)	129
two Ge atoms: Ge(T2)-O-Si(T2)-O-Ge(T2)	118
two Ge atoms: Ge(T2)-O-Ge(T5)	123

2. Verification of the calculation methods

Li and co-workers have tested the ONIOM2 and ONIOM3 schemes as well as fully optimized cluster model with different sizes and concluded that the small 8T high-level region

along with a suitable sized medium-layer region (ONIOM3) could give reasonable structural and energetic parameters with much less computation cost.^{4–5} For the huge size of 79T cluster of ITQ-13, ONIOM3 scheme is suitable to describe the structural and energetic parameters with reasonable accuracy and computation cost.

To validate our high layer relaxed model within the 79T cluster, the fully relaxed model was also comparatively tested, where all atoms are relaxed and only H atoms of the terminal Si-H dangling bonds are fixed in the space to avoid any unrealistic distortions of the model during the geometry optimization, as given in Table 3.

Table S3 A comparison between the high-layer relaxed model and the fully relaxed 79T model in the calculated adsorption enthalpy (ΔH_{ads}) of methanol and intrinsic free energy barriers (ΔG_{int}^{\neq}) for the methylation (M1 step) in the alkene cycle, the gem-methylation of 2MB \rightarrow 3MB⁺ in the aromatic cycle and the methylation (M1 and M3 steps) in the 2MN based aromatic cycle for MTO over the H-ITQ-13 zeolite at 673.15 K

reaction step	$\Delta H_{\rm ads}$ or $\Delta G_{\rm int}^{\neq}$ (kJ mol ⁻¹)		
	high-layer relaxed model	fully relaxed model	
CH ₃ OH adsorption	-131	-131	
M1 in the alkene cycle	108	90	
gem-methylation, $2MB \rightarrow 3MB^+$	129	111	
M1 in the 2MN based aromatic cycle	125	114	
M3 in the 2MN based aromatic cycle	166	150	

For the adsorption of CH₃OH, both the fully relaxed model and the high layer relaxed model give the same adsorption enthalpy (-131 kJ mol⁻¹). For the M1 reaction step in the alkene cycle, the intrinsic free energy barriers calculated by the fully relaxed model and the high layer relaxed model are 108 and 90 kJ mol⁻¹, respectively. For the gem-methylation of $2MB \rightarrow 3MB^+$, they are 129 and 111 kJ mol⁻¹, respectively. The energy difference between the gem-methylation of $2MB \rightarrow 3MB^+$ and M1 methylation by using the fully relaxed model

is the same as that by using the high-layer relaxed model, viz., 21 kJ mol⁻¹. All these suggest that the high layer relaxed model used in this work can appropriately describe the energy difference between various reaction steps and hence the reaction behavior of MTO over the zeolite catalysts.

3. Appropriate polyMB species as the hydrocarbon pool species

To identify the appropriate polymethylbenzenenes (polyMBs) intermediates in the zeolite pores, it is crucial to consider their Gibbs free energy of formation. The formation Gibbs free energies ($\Delta_r G_n$) of polyMBs were calculated on the basis of the reaction formula:

$$ZOH + (6+n)CH_3OH(g) = ZOH \cdot C_6H_{6-n}(CH_3)_n + (6+n)H_2O(g) + 3H_2(g)$$

where methanol is the only starting material, which interacts with zeolite (ZOH) and forms polyMBs; *n* is the number of the methyl groups on the benzene ring. To make the reaction mass balance, molecular H₂ is used as a gaseous product; however, the contribution of H₂ is a constant and has no effect on the relative energies. The calculated $\Delta_r G_n$ values given in Table S4 allow the discrimination of the preferred intermediates, that is, the species with a more negative $\Delta_r G_n$ value is more preferred as an intermediate in the reaction networks.

Table S4 Adsorption enthalpies (ΔH_{ads}) of various reactant species on H-ITQ-13 at 673.15 K and their formation Gibbs free energies ($\Delta_r G_n$).

adsorbate	$\Delta H_{\rm ads} ({\rm kJ} \; {\rm mol}^{-1})$	$\Delta_{\rm r}G_n$ (kJ mol ⁻¹)	
2MB (p-xylene)	-119	-527	
3MB (1,2,4-trimethylbenzene)	-106	-577	
4MB (1,2,3,5-tetramethylbenzene)	-134	-652	
5MB (pentamethylbenzene)	-130	-676	
6MB (hexamethylbenzene)	-112	-645	

The adsorption enthalpies of various polyMBs on H-ITQ-13 at 673.15 K are also given in Table S4, which illustrates that the adsorption of 1,2,3,5-tetramethylbenzene (4MB) and pentamethylbenzene (5MB) is stronger than that of other polyMBs. Meanwhile, the free energies for the formation of various polyMBs, as also given in Table S4, suggest that the formation of 4MB, 5MB, and hexamethylbenzen (6MB) over H-ITQ-13 are thermodynamically more favorable than para-xylene (2MB) and 1,2,4-trimethylbenzene (3MB).

Taking the methylation and gem-methylation of various polyMBs also into accounts, as discussed in the Main Manuscript, it is quite reasonable to assume that 5MB is easily formed over H-ITQ-13, which should be one of the most favorable HCP species for MTO via the aromatic cycle.

4. About the 6MB based aromatic cycle

The 6MB based aromatic cycle was also considered, as summarized in Scheme S1, Table S5, and Fig. S2.



Scheme S1 Proposed 6MB based aromatic cycle for MTO over H-ITQ-13 zeolite (side-chain route; R represents H for ethene formation and methyl for propene formation).

Table S5 Calculated intrinsic free energy barriers (ΔG_{int}^{\neq}) , reaction free energies (ΔG_r) , relative rate coefficients (*k*), enthalpy barriers (ΔH_{int}^{\neq}) , and entropy losses $(-T\Delta S_{int}^{\neq})$ of each reaction step via the 6MB based aromatic cycle (side-chain route) for MTO at 673.15 K over the H-ITQ-13 zeolite.

reaction step	$\Delta G_{ m int}^{ eq}$ (kJ mol ⁻¹)	$k (s^{-1})$	$\Delta H_{\rm int}^{\neq}$ (kJ mol ⁻¹)	$-T\Delta S_{\text{int}}^{\neq}$ (kJ mol ⁻¹)	$\Delta G_{\rm r}$ (kJ mol ⁻¹)
M1	109	5.20×10 ⁴	99	10	38
M2	183	9.30×10 ⁻²	164	19	35
ethene formation					
J1(e)	108	5.67×10 ⁴	101	7	-10
J2(e)	93	9.14×10 ⁵	72	21	-14
J3(e)	70	5.65×10 ⁷	63	7	-132
E(e)	163	2.89×10 ⁰	162	1	-130
propene formation					
M3	150	3.37×10 ¹	139	11	-8
J1(p)	106	8.79×10 ⁴	96	10	-9
J2(p)	107	7.09×10 ⁴	88	19	2
J3(p)	105	1.07×10 ⁵	97	8	-104
E(p)	-	-	-	-	-

In comparison with the 5MB based aromatic cycle, the intermediates of 6MB cycle are rather unstable with high free energies, due to the severe repulsion between 6MB molecule and the zeolite framework. In practice, it was very difficult to find the transition state for propene elimination step E(p). The ultimate free energy barrier (ΔG_{ult}^{\neq}) of 6MB based aromatic cycle, viz., the free energy difference between the transition state of M2 and the reference state along the free energy surface, is 298 kJ mol⁻¹, much higher than that of 5MB based aromatic cycle (246 kJ mol⁻¹). All these suggest that 6MB as the HCP species is less active than 5MB for MTO over H-ITQ-13 to yield ethene and propene.



Fig. S2 Free energy profiles for the formation of olefins via 6MB based aromatic cycle for MTO over the H-ITQ-13 zeolite at 673.15 K. The zeolite framework as well as the methanol and 6MB in gaseous phase are taken as the reference state. Water molecule formed in the methylation step is released as gaseous species before methyl-shift step.

References

- D. Lesthaeghe, B. De Sterck, V. Van Speybroeck, G. B. Marin and M. Waroquier, *Angew. Chem. Int. Ed.*, 2007, 46, 1311–1314.
- D. M. McCann, D. Lesthaeghe, P. W. Kletnieks, D. R. Guenther, M. J. Hayman, V. Van Speybroeck, M. Waroquier and J. F. Haw, *Angew. Chem. Int. Ed.*, 2008, 47, 5179–5182.
- (3) L. Li, Y. Chen, S. Xu, J. Li, M. Dong, Z. Liu, H. Jiao, J. Wang and W. Fan, J. Catal., 2016, 344, 242–251.

- (4) Y. Li, W. Guo, S. Yuan, W. Fan, J. Wang and H. Jiao, J. Mol. Struct. THEOCHEM, 2009, 916, 53–60.
- L. W. Chung, W. M. C. Sameera, R. Ramozzi, A. J. Page, M. Hatanaka, G. P. Petrova,
 T. V. Harris, X. Li, Z. Ke, F. Liu, H. B. Li, L. Ding and K. Morokuma, *Chem. Rev.*,
 2015, 115, 5678–5796.