

Supporting Information

Establishing a Link between the Dual Cycles in Methanol-to-Olefins Conversion on H-ZSM-5: Aromatization of Cycloalkenes

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1. Methods

1.1 X-ray power diffraction (XRD)

The structure and crystalline nature of H-ZSM-5 zeolites (Si/Al = 23, zeolyst) were examined by X-ray diffractometer (X'Pert³ Powder) using a CuK α radiation with a step of 0.02 ° at a respective voltage of 40 kV and a current of 40 mA. The scanning range was 5 ° to 40 °.

1.2 FT-IR of pyridine adsorption.

The FT-IR of pyridine adsorption measurements were performed on a Bruker Tensor 27 spectrometer. The catalysts were first activated at 673 K under high vacuum ($<10^{-5}$ Pa) for 10 h. After cooling down to 307 K, a background spectrum was collected. Excessive amount of pyridine was then introduced to the infrared cell and held for 2 h to allow equilibrium. The residual pyridine was removed by vacuum. The FT-IR spectra of pyridine-adsorbed samples were measured at 313 K after evacuation at 423, 623, and 723 K, respectively.

1.3 Catalytic testing.

All catalytic reactions were carried out in a pulse quench reactor¹ with inner diameter of 6 mm. The H-ZSM-5 powder was pressed into pellets between 40-60 mesh. The pellets (0.1 g) were activated at 400 °C in flowing helium for 1 h prior to the reaction. The total gas flow through the reactor was 200 sccm. Then the reaction was thermally quenched by pulsing liquid nitrogen onto the catalyst bed, and the temperature was cooled down from reaction temperature to ambient temperature within a very short

period (0.2 s), which was achieved using high-speed valves controlled by a GC computer. In each case, a certain amount of reactant was pulsed into the reactor containing 0.1 g H-ZSM-5 and reacted for predetermined time at predetermined temperature. The retained products were analyzed by ^{13}C solid-state NMR spectroscopy and the effluent products were determined by GC-MS analysis online after the pulse quench reaction. The retained products were also analyzed by GC. Namely, the zeolites with trapped species was dissolved in 1.5 ml 20 wt. % HF solution and then extracted with 1 ml CH_2Cl_2 . After uniformly shaking and mixing, standing for 2 minutes, the bottom layer, containing the organic phase of the extracted solution, was separated and analyzed by gas chromatography.

1.4 Gas chromatography

The effluent was analyzed by online GC-MS (Shimadzu GCMS-QP2010) equipped with a Petrocol DH 100 capillary column (100 m, 0.25 mm i.d., 0.5 μm film thickness). The temperature programming started at 40 $^\circ\text{C}$ (maintained for 2 min), followed by a rate of 1 $^\circ\text{C min}^{-1}$ to a temperature of 50 $^\circ\text{C}$ (maintained for 2 min) and a rate of 15 $^\circ\text{C min}^{-1}$ to a final temperature of 250 $^\circ\text{C}$. The isotopic compositions of the trapped species were also analyzed by GC-MS (Shimadzu GCMS-QP2010) equipped with the same capillary column. The following temperature programming was applied: an initial temperature of 50 $^\circ\text{C}$ was maintained for 1 min, followed by a rate of 10 $^\circ\text{C min}^{-1}$ to a final temperature of 250 $^\circ\text{C}$.

1.5 Solid-State NMR experiments

After the reaction was quenched, the reactor containing the catalyst was cooled down

and sealed with valves. The sealed reactor was then transferred to a glove box filled with pure N₂ and the catalyst was packed into an NMR rotor for NMR measurements. All the ¹³C solid-state NMR experiments were carried out at 9.4 T on a Bruker Avance III-400 spectrometer, equipped with a 4 mm probe, with resonance frequencies of 399.33 and 100.42 MHz for ¹H and ¹³C, respectively. The magic angle spinning rate was set to 10 kHz. For the ¹H → ¹³C CP/MAS NMR experiments, the Hartmann-Hahn condition was achieved using hexamethylbenzene (HMB), with a contact time of 5 ms and a repetition time of 2 s. The ¹³C chemical shifts were referenced to HMB (a second reference to TMS). The ²⁷Al MAS NMR spectra were acquired on the same 4 mm probe using small-flip angle technique with a pulse length of 0.3 μs (<π/12) and a recycle delay of 1 s. The magic angle spinning rate was set to 10 kHz. The ²⁷Al chemical shifts were referenced to 1 M Al(NO₃)₃ aqueous solution (0 ppm). ²⁹Si MAS NMR spectra were acquired with high power proton decoupling on the 4 mm probe, using a π/2 pulse of 5.3 μs, a recycle delay of 80s and a spinning rate of 10 kHz. The ²⁹Si chemical shifts were referenced to kaolinite (−91.5 ppm).

1.6 Computational method:

For the reaction route calculation, the H-ZSM-5 zeolites is represented by a 72T model, which was extracted from its crystallographic structural data (<http://www.iza-structure.org/databases/>). The 72T contains the complete double 10-MR intersection pores of ZSM-5 zeolite. The terminal Si–H was fixed at a bond length of 1.47 Å, oriented along the direction of the corresponding Si–O bond. Based on the previous work², the Al atom is located at the T12 site for H-ZSM-5. The 24T active site atoms

and the adsorbed hydrocarbon complex were treated as the high-layer (See Figure S12) while the rest of the frameworks were treated as the low-layer. To retain the structural integrities of the modeled zeolite, partial structure optimizations of the 72T cluster were performed by relaxing the atoms in the the high-level layer while keeping the rest of atoms fixed at their crystallographic positions. All the TS structures are found by the QST3 method in the Gaussian program. Then based on the imaginary vibrational model of the optimized TS, we adjusted the positions of the vibrational atoms slightly along the calculated reaction coordinate on the two directions toward the reactant and product, respectively, and finally optimized the resulting structures to the minimum structures. These methods have been widely employed in other previous theoretical work³⁻⁴.

A combined theoretical approach, namely ONIOM (wb97xd/6-31G(d,p): am1) was used for the geometry optimization of adsorption states and transition states (TS). The ω B97XD hybrid density function was developed to consider long-range-corrected hybrid functional, which implicitly accounted for empirical dispersion and could describe long-range dispersion interactions well with respect to the traditional density functional theory methods⁵. This functional was also recently found to perform very well for the description of adsorption and reactions on zeolites. All energies report herein were predicted at the WB97XD/6-31G(d,p) level based on the optimized structures. The frequency calculations were performed at the same level as geometry optimizations to check whether the stationary points found exhibit the proper number of negative frequencies. Only one negative frequency would be observed for transition state point and none for the corresponding reactant and product.

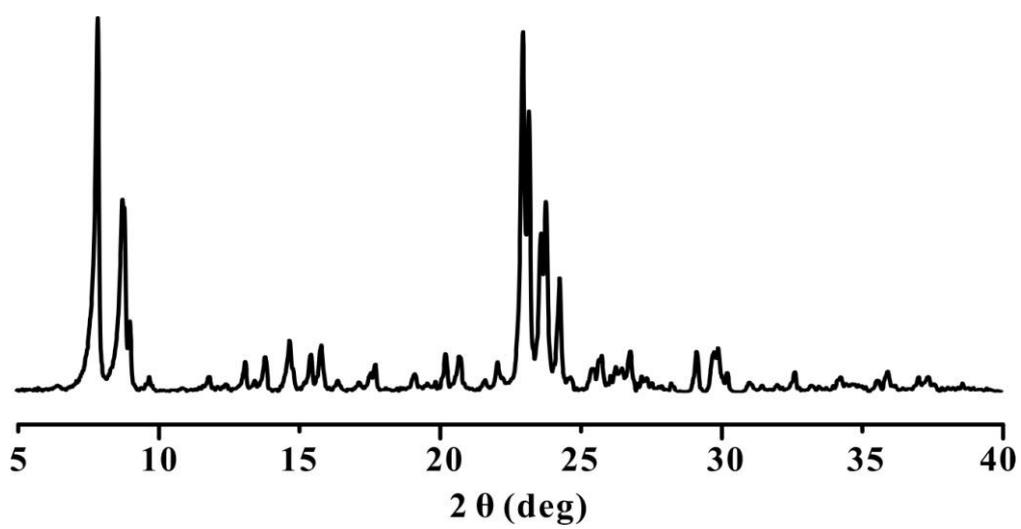


Figure S1. XRD pattern of H-ZSM-5.

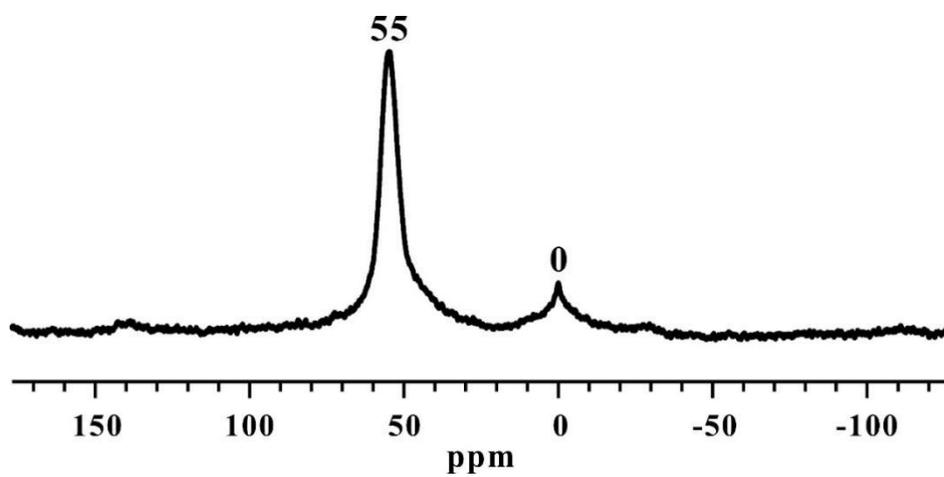


Figure S2. ^{27}Al MAS NMR spectrum of H-ZSM-5.

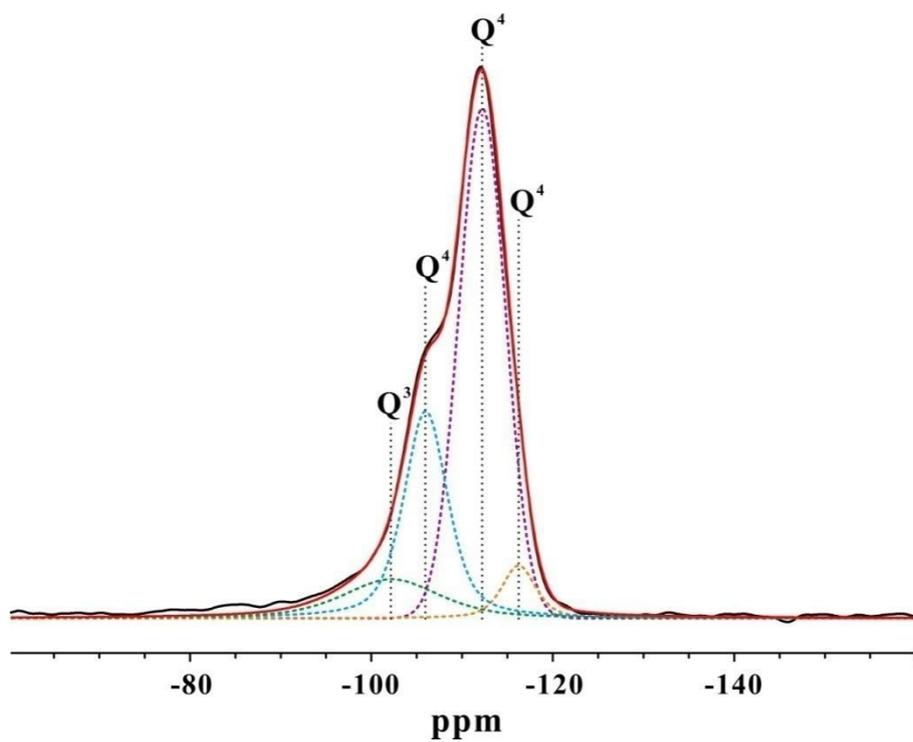


Figure S3. ^{29}Si MAS NMR spectrum of H-ZSM-5.

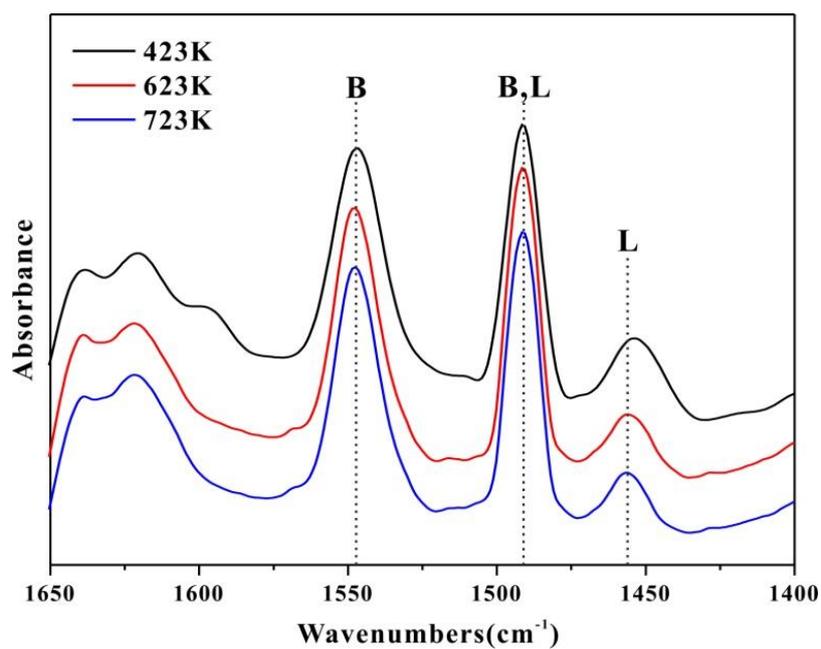


Figure S4. FT-IR spectra of pyridine adsorbed on H-ZSM-5 after evacuation at different temperatures. The B, L peaks represent Brønsted acid sites and Lewis acid sites respectively.

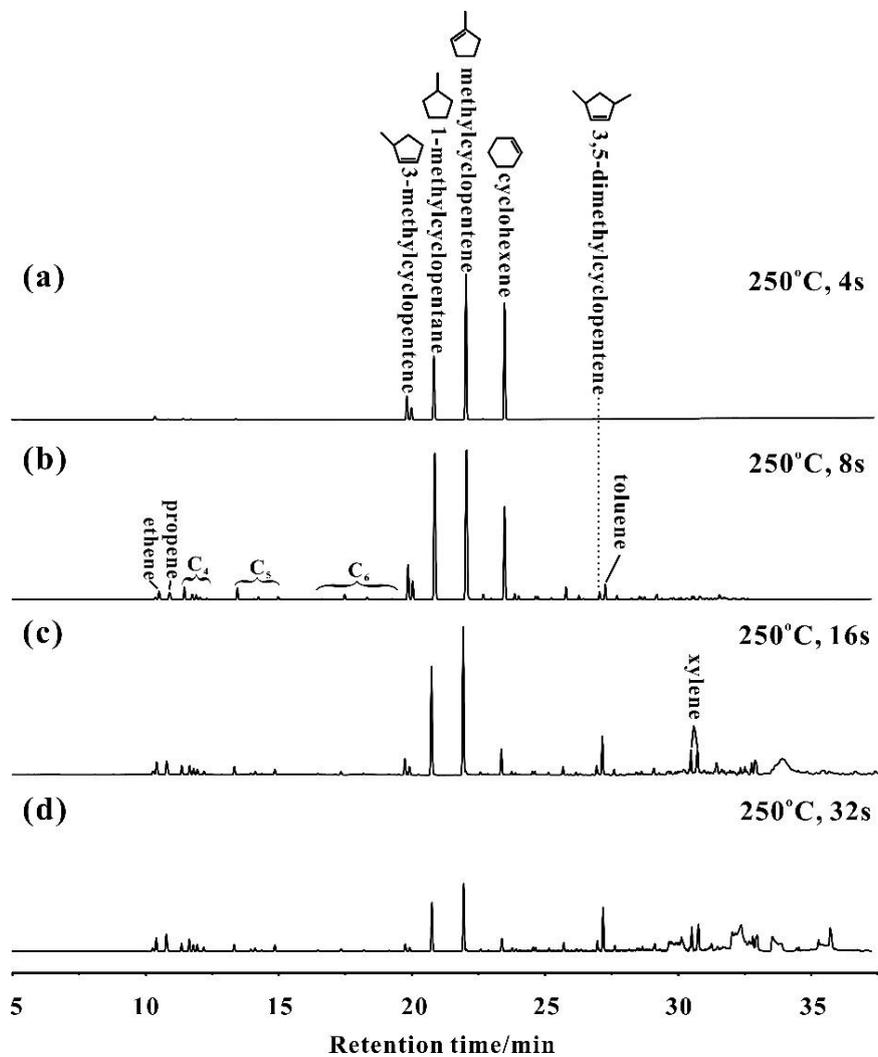


Figure S5. Gas chromatography analysis of the effluent products obtained from reaction of cyclohexene over H-ZSM-5 at 250 °C for 4 s-32 s (a-d)

Table S1. Product selectivity (C%) and cyclohexene conversion (%) obtained from pulse reaction of cyclohexene on H-ZSM-5 at 250°C for different time.

RT(s)	Con.	C2	C3	C4	C5	C6	Five-membered ring compounds	C ₆₊ aromatics
4	67.97	1.43	0.07	0.60	0.30	0.07	97.52	0.00
8	83.46	1.78	1.94	4.92	3.52	1.85	82.19	3.81
16	94.73	2.94	3.72	6.99	4.04	1.62	62.26	18.43
32	96.85	4.38	6.60	11.08	6.30	0.97	43.50	27.15

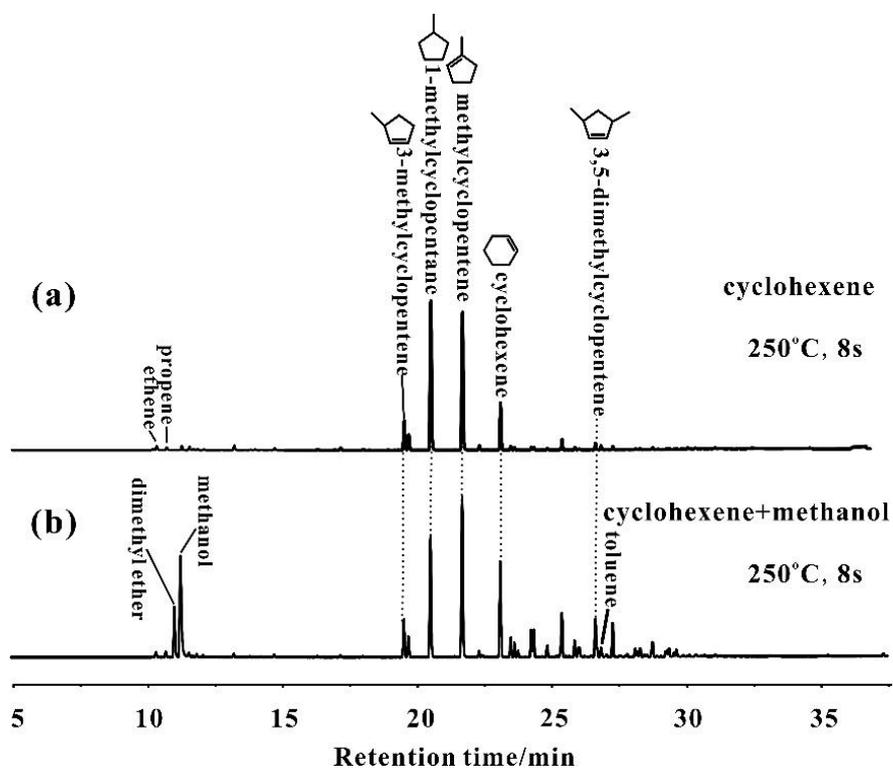


Figure S6. Gas chromatography analysis of the effluent products obtained from reaction of cyclohexene alone (a) and co-feeding cyclohexene/methanol mixture (b) over H-ZSM-5(Si/Al=50) at 250 °C for 8 s.

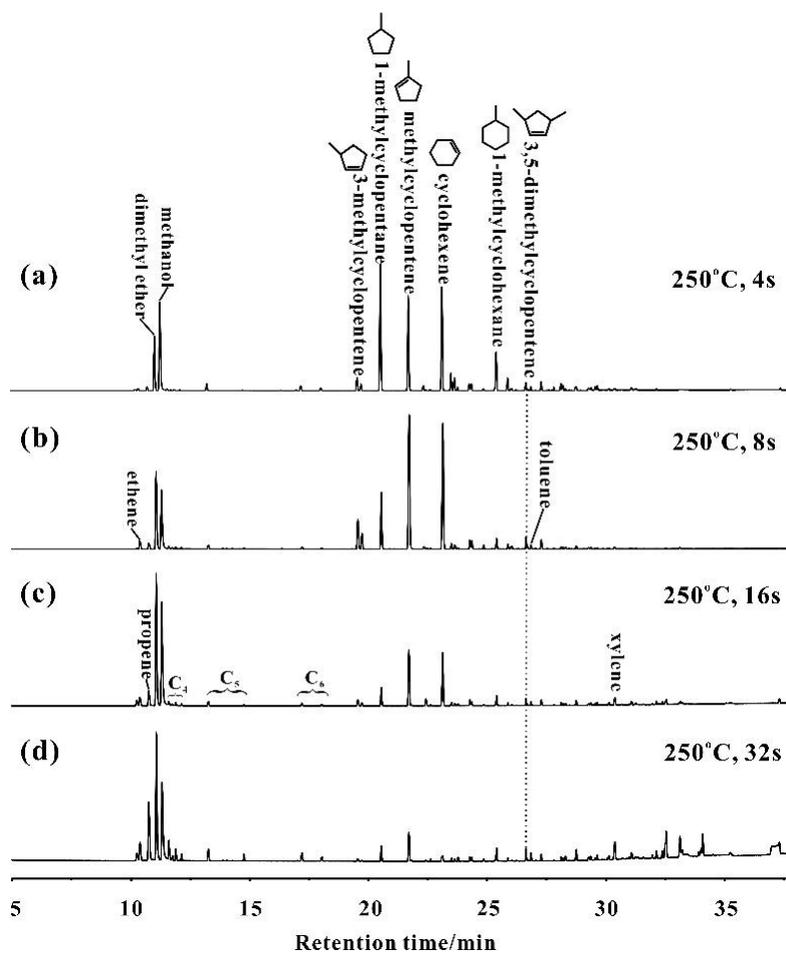


Figure S7. Gas chromatography analysis of the effluent products obtained from co-reaction of cyclohexene with methanol over H-ZSM-5 at different temperatures for 8 s.

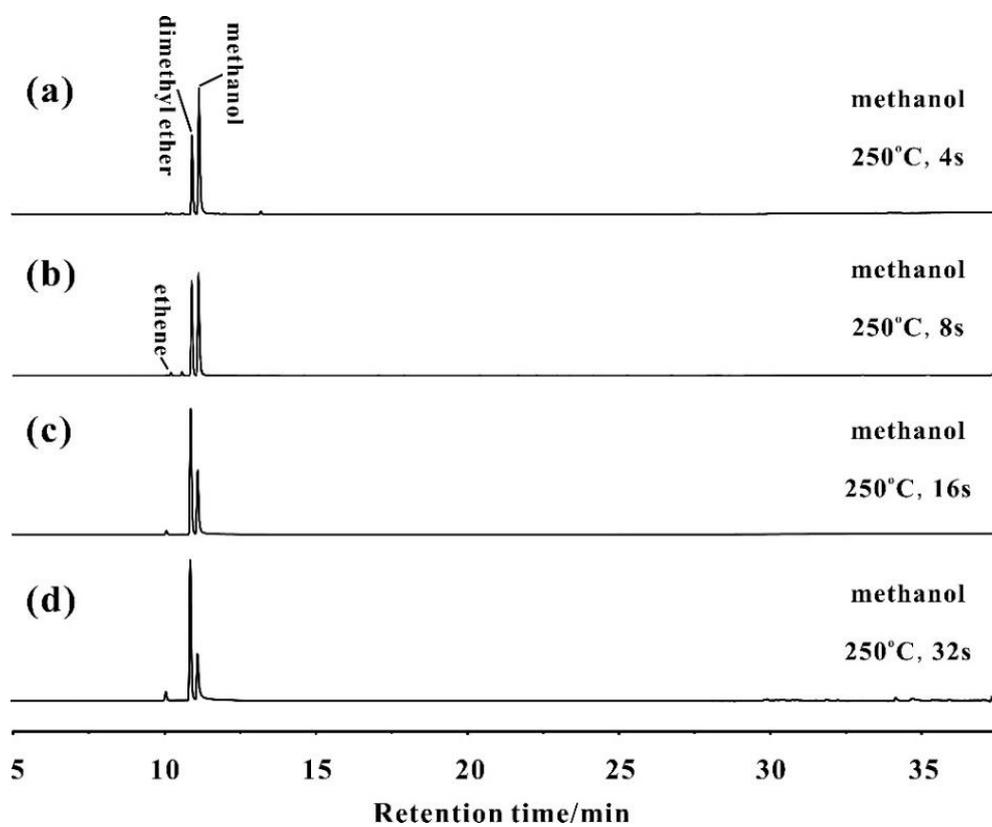


Figure S8. Gas chromatography analysis of the effluent products obtained from reaction of methanol over H-ZSM-5 at 250 °C for different time.

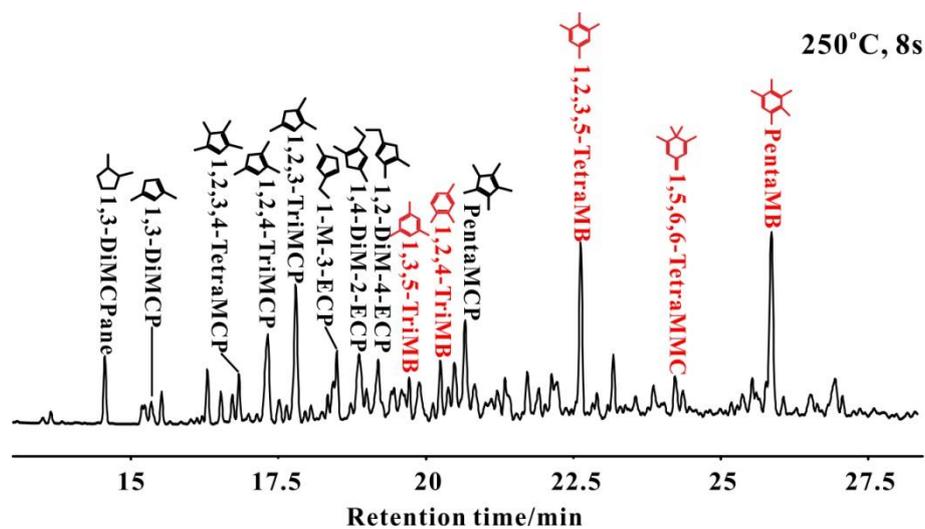


Figure S9. Gas chromatography analysis of trapped organic species obtained from cofeeding cyclohexene and ^{13}C -methanol on H-ZSM-5 zeolites at 250 °C for 8 s.

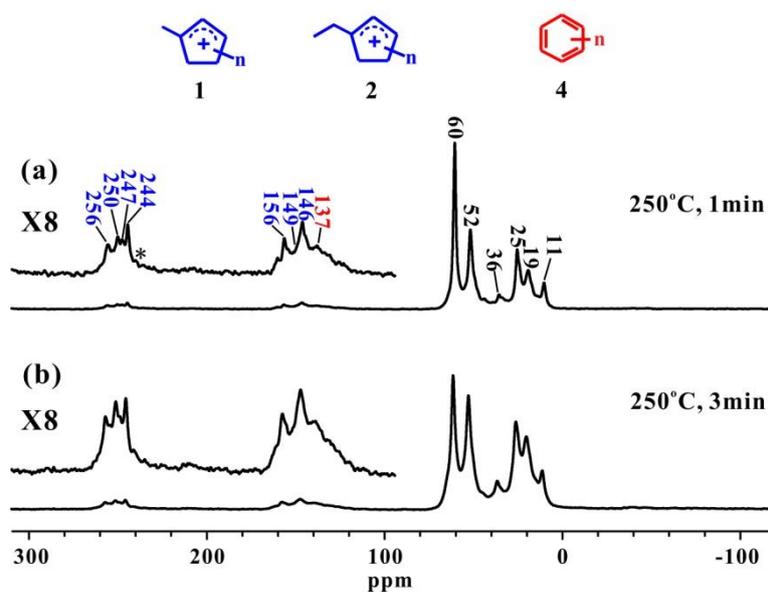


Figure S10. ^{13}C CP MAS NMR spectra of trapped species on H-ZSM-5 obtained from co-reaction of cyclohexene with ^{13}C -methanol at 250 °C for 1 min (a) and 3 min (b).

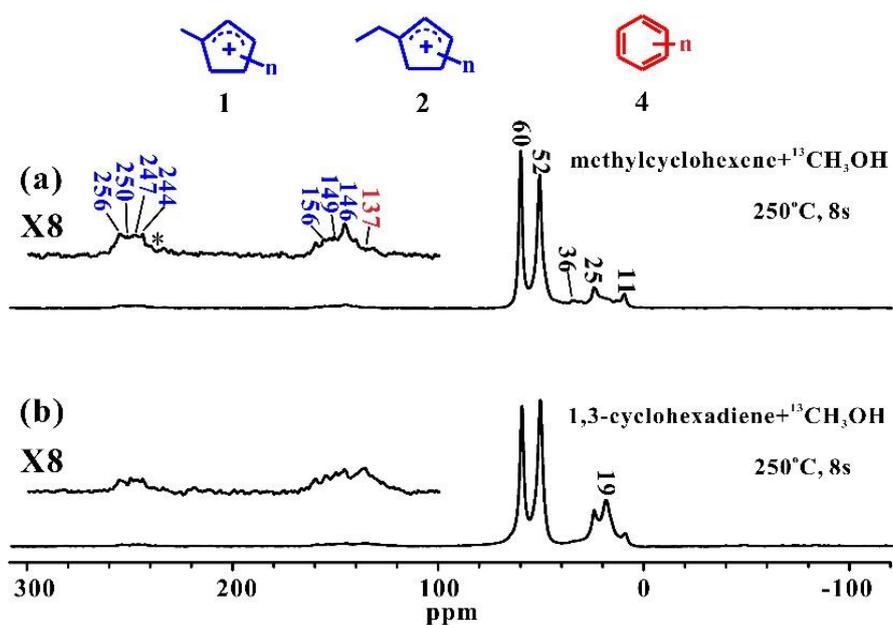


Figure S11. ^{13}C CP MAS NMR spectra of trapped species on H-ZSM-5 obtained from co-reaction of 1-methylcyclohexene with ^{13}C -methanol (a) and 1,3-cyclohexadiene with ^{13}C -methanol (b) at 250 °C for 8 s.

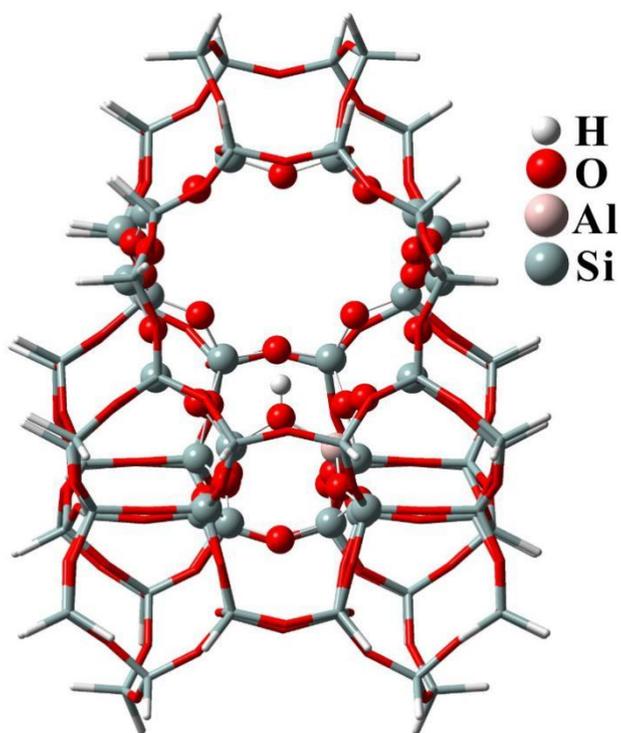


Figure S12. Representation of the H-ZSM-5 zeolite framework by a 72T cluster model represented as ball and stick view. The 24T cluster model in the extended model represents the acid site of the zeolite which is treated as the high-layer atoms during the ONIOM calculations.

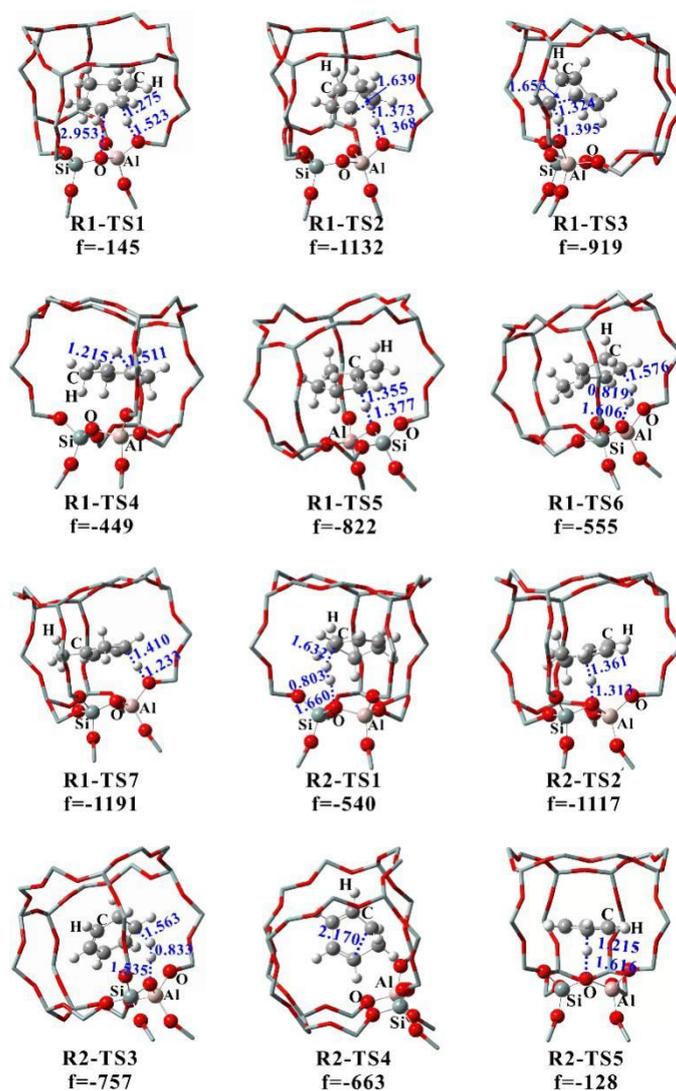
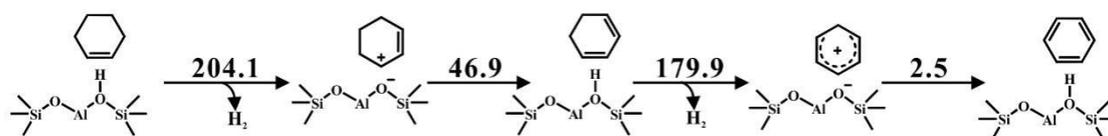


Figure S13. Optimized transition state (TS) structures for the formation of benzene in H-ZSM-5 zeolite following the aromatization route of cyclohexene (See Scheme 1 and Scheme S1). The main geometric parameters and the imaginary frequency (f) are labeled in Å and cm^{-1} .

Direct dehydrogenation



Scheme S1. Elementary steps in the proposed route for direct dehydrogenation of cyclohexene over H-ZSM-5. The calculated activation energy barriers in kJ/mol are also given for each step.

References

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