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Influence of zeolite confinement effects on cation-π interactions in methanol-to-hydrocarbons conversion

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Experimental section

Catalysts characterization

The elemental composition was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Agilent ICPOES730). The Powder X-ray diffraction (XRD) was performed on a PANAlytical X'Pert Powder X-ray diffraction diffractometer with Cu Kα (λ=1.5406 Å), recording at 40 kV and 40 mA. The NH_3-TPD measurements were performed using a FINESORB-3010 chemisorption instrument. Typically, 100 mg of sample was pre-treated at 773 K for 2 h under 25 sccm of He. After the sample cooled down to 373 K, NH_3 was introduced and held for 1 h. The temperature was then elevated from 373 to 873 K at a ramping rate of 10 K/min and the desorbed NH_3 was detected by a thermal conductivity detector (TCD).

Cyclopentenyl cation containing samples

The H-ZSM-5 (Si/Al=11.62) and H-β (Si/Al=10.24) powder was pressed into pellets between 60-80 mesh, which were activated at 400 °C (ramp rate of 2 ^{o}C/min) in flowing helium for 1 h prior to reaction. The cyclopentenyl cation containing samples were prepared by reacting ^{13}C methanol (99%) under continuous flow condition at 300 ^{o}C. 0.2 g catalyst pellets was equally divided into two parts (layers) by glass wool in the fixed bed reactor[1]. Methanol with a partial pressure of 5 kPa was reacted over the catalytic bed. The total gas flow through the reactor was 100 sccm. After methanol reacted for 15 min, the catalytic bed was thermally quenched by liquid nitrogen. The cyclopentenyl cations were found to be dominant in the lower part of the catalyst bed.[1] Therefore the first H-H-ZSM-5 and H-H-β bed layer in reactor was removed and

the second layer was used for NMR investigation.

Adsorption of benzene molecules

Before adsorption of benzene, the cyclopentenyl cation containing H-ZSM-5 and H-β zeolites were initially degassed at room temperature under vacuum environment (at a pressure of 10^{-3} Pa for 2h). 0.1 kPa ^{13}C benzene ($^{13}C_6$, 99%) were adsorbed onto the cyclopentenyl cation containing H-ZSM-5 or H-β in a glass tube under vacuum at ambient temperature. The glass tube containing the adsorbed sample was sealed off from the vacuum system under the protection of liquid nitrogen. Then the obtained sample was packed into a 4 mm rotor in a glove box filled with pure N_2 for NMR experiments.

Catalytic experiments

For the analysis of the role of cyclopentenyl cations, methylcyclopentene (98%) was used as the precursor to produce cyclopentenyl cations during the reations. The co-reaction of methylcyclopentene and benzene was conducted at pulse-quench reaction condition[2]. This type of reactor allows the reactions to be quenched by liquid N_2 within 200 ms. The active surface can be quickly fossilized on catalyst and the volatile products can be simultaneously analyzed by on-line GC. A high carrier gas flow up to 200 sccm was applied, which enabled a fast introduction of the reactant and quickly took away the products on seconds scale. The mixtures of 10 μl methylcyclopentene and 10 μl benzene were pulsed over 0.2 g H-ZSM-5 or H-β pellets for 8 s reaction and then thermally quenched by liquid nitrogen. The retained products were dissolved in 20 wt% HF solution and then extracted with CH_2Cl_2. The

extracts were analyzed by GC-MS.

Reaction product analysis

The extracts from the co-reaction of methylcyclopentene and benzene were analyzed by GC-MS (Shimadzu GCMS-QP2010) equipped with the capillary column Petrocol DH 100 (100 m, 0.25 mm i.d., 0.5 μm film thickness). The following temperature programming was applied: maintained at an initial temperature of 50°C for 1 min, followed by a rate of 10°C min^{-1} to a finial temperature of 250 °C (maintained for 30 min).

UV-Vis experiments

The UV-vis diffuse reflectance spectra of zeolites were recorded in the wavenumber of 200 nm-800 nm over an Agilent Cary 4000 UV-vis spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated with $BaSO_4$. Unreacted H-ZSM-5 zeolite was used as reference. The scanning rate was 300 nm/min at a bandwidth of 2 nm through dual-beam mode.

Solid-state NMR experiments

All solid-state NMR experiments were performed at 11.7 T on a Bruker-Avance III-500 spectrometer, equipped with a 4 mm probe, with resonance frequencies of 500.57 and 125.87 MHz for ^{1}H and ^{13}C, respectively. For the ^{1}H MAS NMR experiments, single-pulse excitation was performed using a ^{1}H $\pi/2$ pulse length of 3.7 μs and a repetition time of 2 s. The ^{1}H chemical shifts were referenced to adamantane (1.78 ppm). Adamantane was used as an external chemical shift reference for ^{13}C by setting the CH_2 resonance to 38.5 ppm. The magic angle spinning rate was set to 10 kHz. For

the $^{1}H \rightarrow ^{13}C$ 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. 512 scans were conduct for each spectrum. 2D ^{13}C-^{13}C PDSD (proton-drive-spin-diffusion) spectra were recorded at 10 kHz MAS. The ^{1}H radiofrequency (rf) field strength for the heteronuclear SPINAL 64 decoupling was 64 kHz. The $\pi/2$ pulse lengths were set at 3.7 and 3.8 us for ^{1}H and ^{13}C, respectively. A 70 % ramp for the ^{1}H CP pulse with a 4.5 ms CP contact time, 2 s recycle delay, 12 ms and 6 ms acquisition times for direct and indirect ^{13}C dimensions, respectively, and 800 ms for the proton-driven spin-diffusion mixing time. A total of 200 scans were conduct for each of the 25 μs rotor-synchronized t1 increments with a recycle delay of 1.0 s. The 2D ^{13}C-^{13}C PDSD spectra were obtained by the covariance transform from FID data[3].

Theoretical calculations

H-H-ZSM-5, H-H-SSZ-13 and H-H-β zeolites are represented by 72T, 74T and 80T models, respectively, which were extracted from their crystallographic structural data (http://www.iza-structure.org/databases/). The 72T contains the complete double 10-MR intersection pores of H-ZSM-5 zeolite (See Figure S4a). The 74T H-SSZ-13 model includes two complete cages connected via an 8-MR window (See Figure S4b). The 80T H-β model has a three-dimensional channel with 12-membered ring apertures (See Figure S4c). 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 studies, the Si12–O24(H)–Al12, Si1–O2(H)–Al1 and Si6-O11(H)-Al4 were chosen as the acid site positions for H-ZSM-5, H-SSZ-13 and H-β, respectively [4-5].

In this work, the active site atoms and the adsorbed hydrocarbon complex were treated as the high-level layer (see Figure S7), while the rest of the frameworks were treated as the low-level layer. To retain the structural integrities of the modeled zeolite, partial structure optimizations were performed by relaxing the atoms in the high-level layer while the framework atoms at the low level of ONIOM calculation were fixed at their crystallographic positions.

A combined theoretical approach, namely ONIOM (M062x/6-311G(d,p): am1) was used for the geometry optimization of adsorption states and transition states (TS). The M062X is a hybrid meta density functional theory (DFT) method developed by Zhao and Truhlar, which accounts for medium-range electron correlation[6]. This functional was also found to perform very well for the description of alkane adsorption and activation on zeolites[7]. Since the AM1 method is believed to underestimate the low-level interaction energies, all energies reported herein were predicted at the M062X/6-311G (d, p) level based on the optimized structures.

All the calculations were performed using the Gaussian 09 package

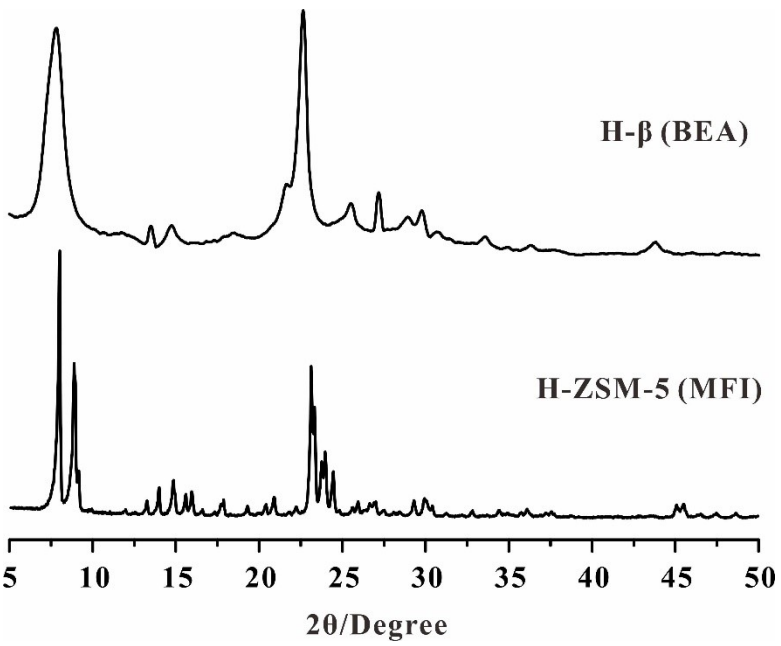

Figure S1. XRD patterns of H-ZSM-5 and H-β.

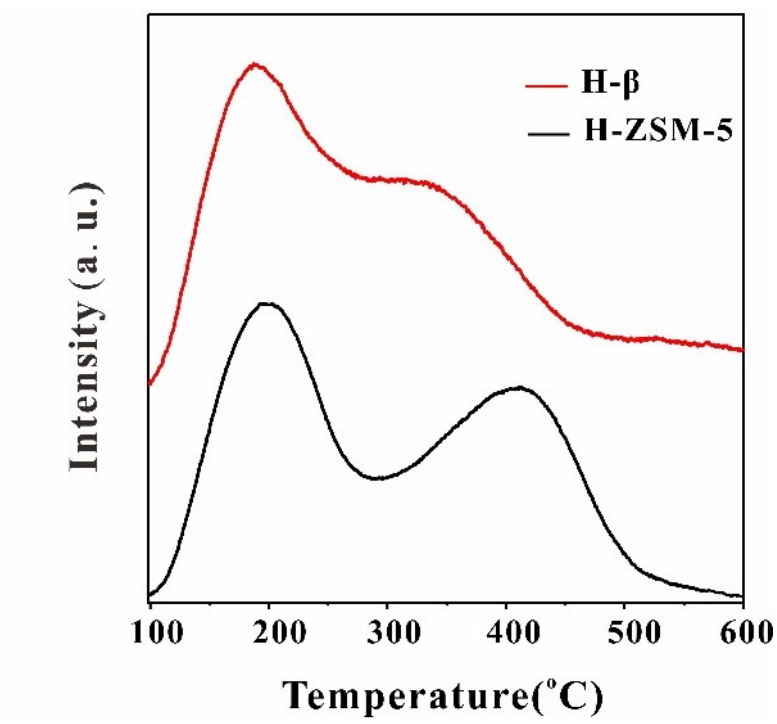

Figure S2. NH_3-TPD curved of H-ZSM-5 and H-β zeolites

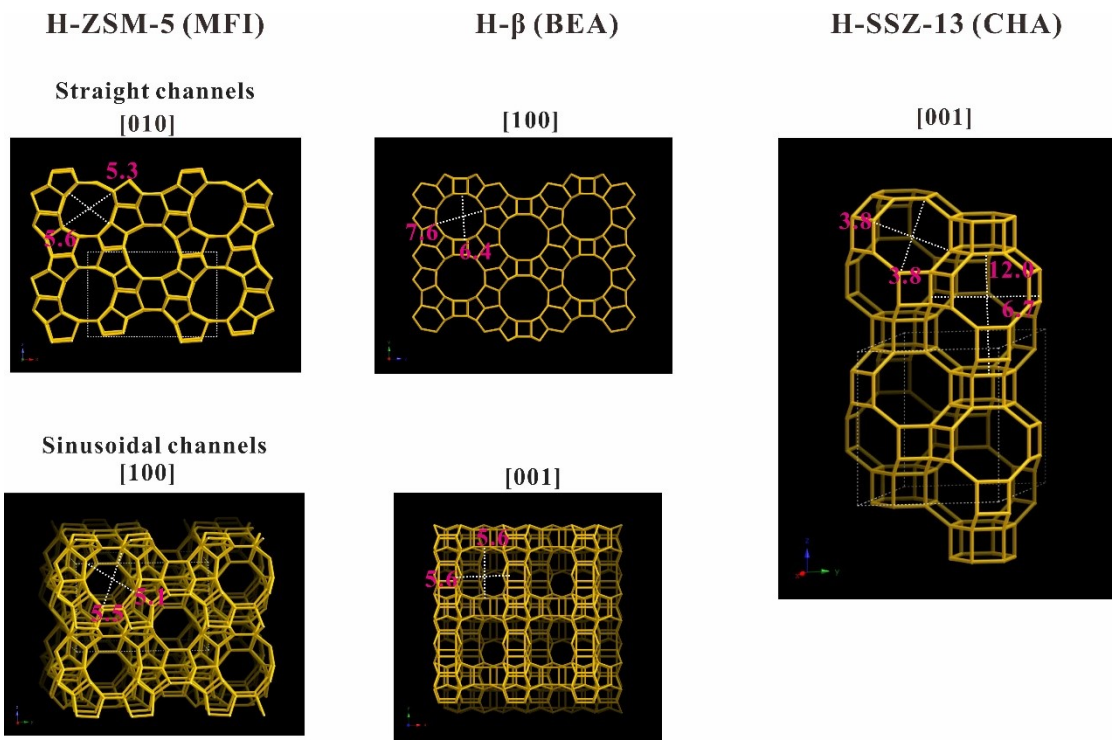

Figure S3. Structures of H-ZSM-5, H-β and H-SSZ-13 zeolites[8]. The size (Å) of the pores and windows of zeolites are indicated.

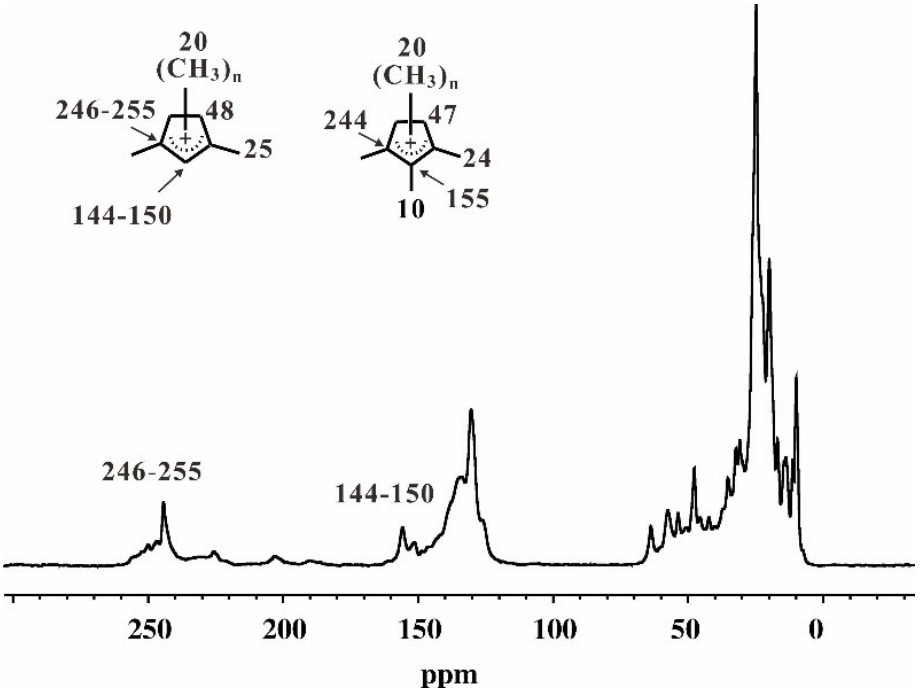

Figure S4. ^{13}C CP MAS NMR spectrum of retained species formed in H-SSZ-13 zeolite after reaction of ^{13}C-methanol at 300 ^{o}C for 15 min

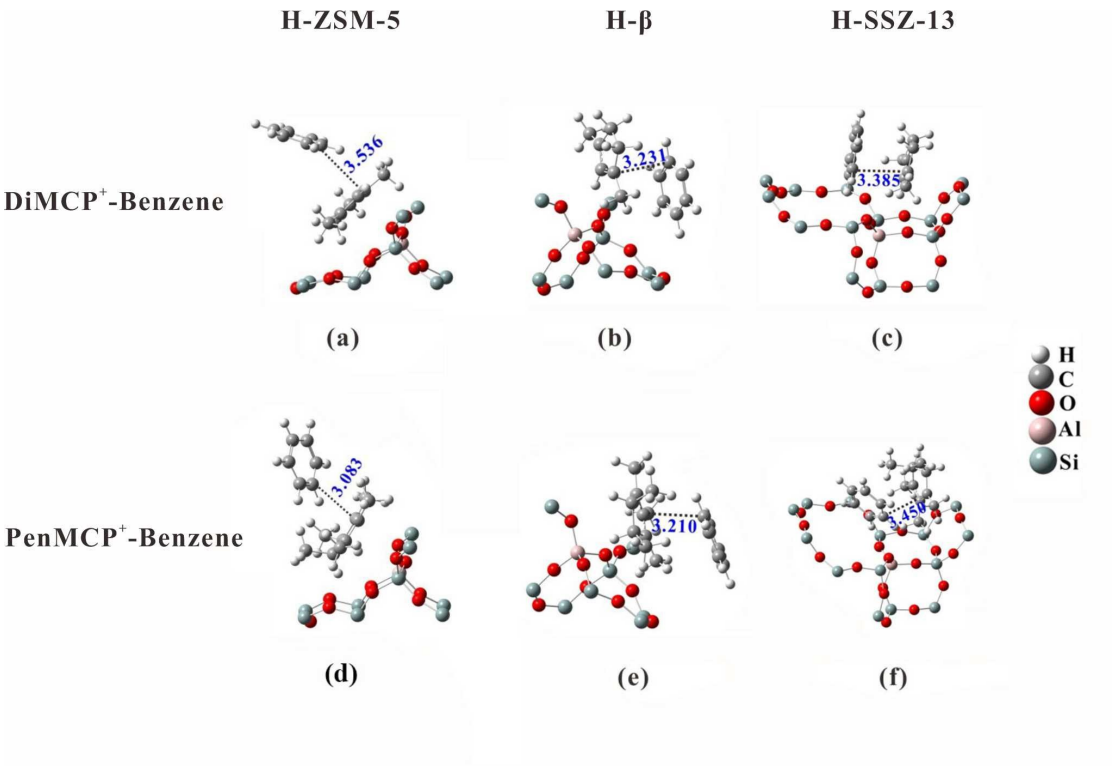

Figure S5. Theoretically optimized local structures of benzene interacting with dimethylcyclopentenyl ($DiMCP^+$) and pentamethylcyclopentenyl cations ($PentaMCP^+$) confined in H-ZSM-5 (a, d), H-β (b, e) and H-SSZ-13 (c, f). The shortest interatomic distances (in Å) are indicated.

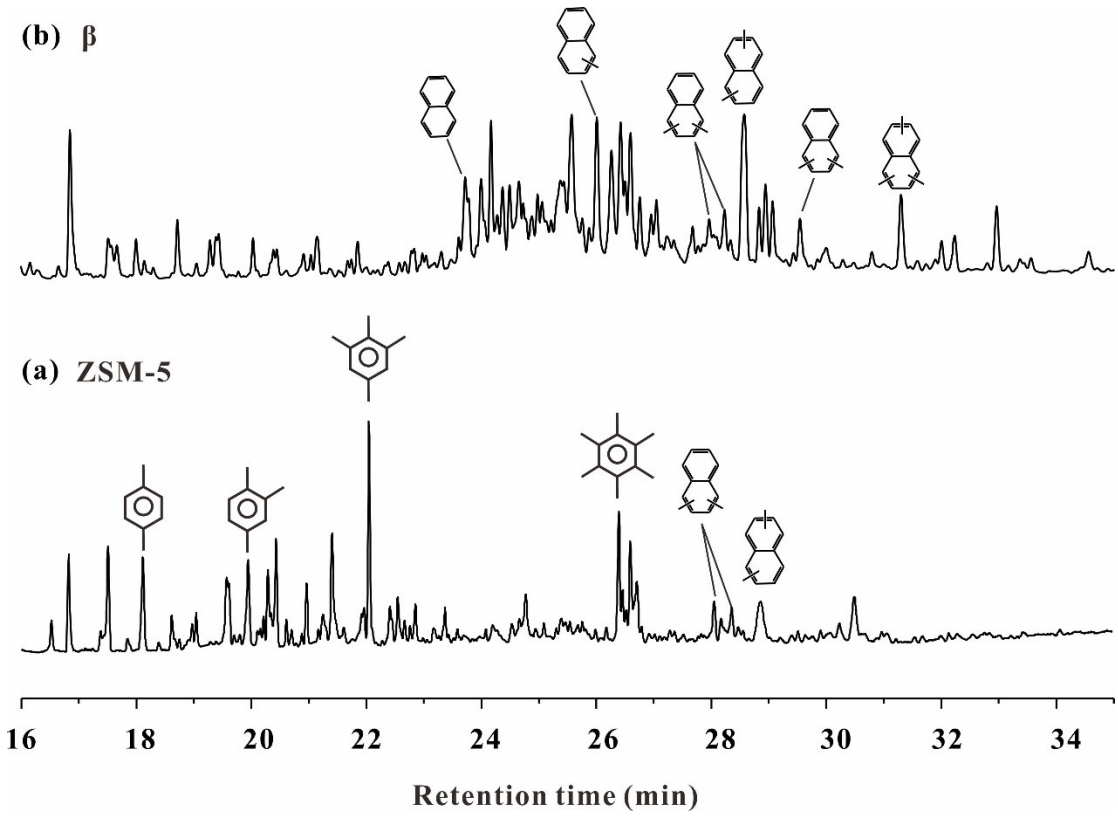

Figure S6. GC-MS spectra of abstracts from H-ZSM-5 (a) and H-β zeolites after co-reaction between benzene and methylcyclopentene at 400 ^{o}C for 8s.

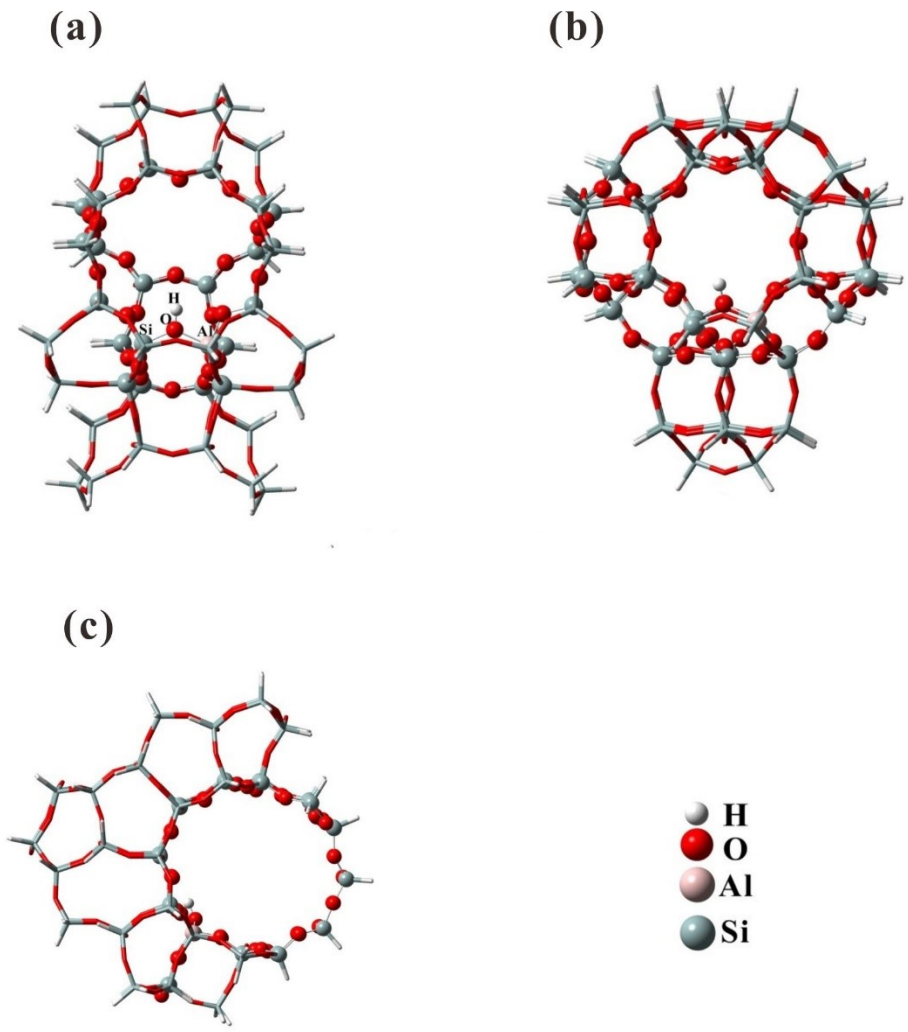

Figure S7. Representation of the H-ZSM-5, H-SSZ-13 and H-β zeolite framework structures by 72T (a), 74T (b), and 80T (c) cluster models. The 24T for H-ZSM-5, 24T for H-SSZ-13 and 28T for H-β represented as a ball and stick view were treated as the high-layer atoms during the ONIOM calculations.

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