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Supplementary Information

A mechanistic model for hydrogen activation, spillover, and its chemical reaction in a zeolite-encapsulated Pt catalyst

Hyeyoung Shin[a], Minkee Choi[b] and Hyungjun Kim*[a]

[a]Graduate School of Energy, Environment, Water, and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), Yuseong-gu, Daejeon 305-701, Korea

[b]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Yuseong-gu, Daejeon 305-701, Korea

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* Corresponding author. Email: linus16@kaist.ac.kr

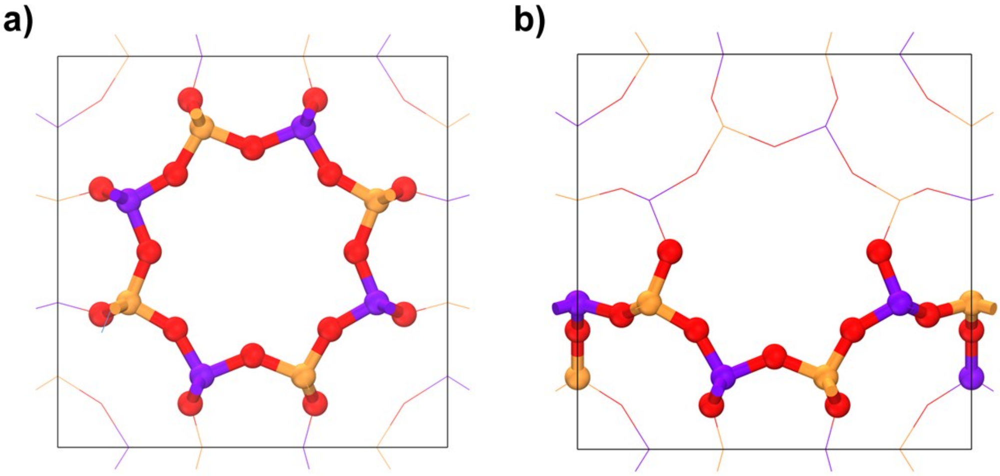

Fig. S1. Atomistic structures used for (a) the ring-shaped zeolite model and (b) the linear chain zeolite model. Each zeolite model is indicated as ball-stick-shape. All models are built based on the experimentally reported NaA structure (ICSD 9326), which is illustrated as a stick shape in both figures. These models have alternative arrangements of four-coordinate Al and Si atoms, which are bridged via either an O atom or an OH group (Brønsted acid site; BAS). The positions of oxygen atoms pointing in outward directions are fixed during the DFT optimization steps. Orange, purple, and red colors represent Si, Al, and O atoms, respectively.

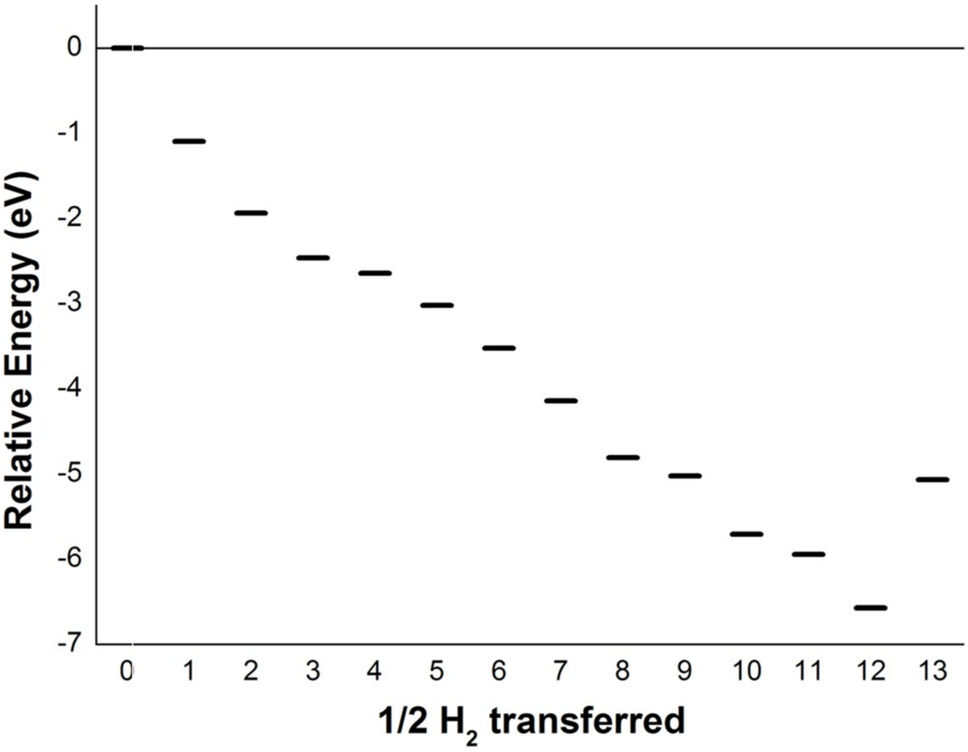

Fig. S2. Energy diagram for sequential hydrogenation steps of the Pt_6 nanoparticle interacting with the zeolite surface (Fig. 1b).

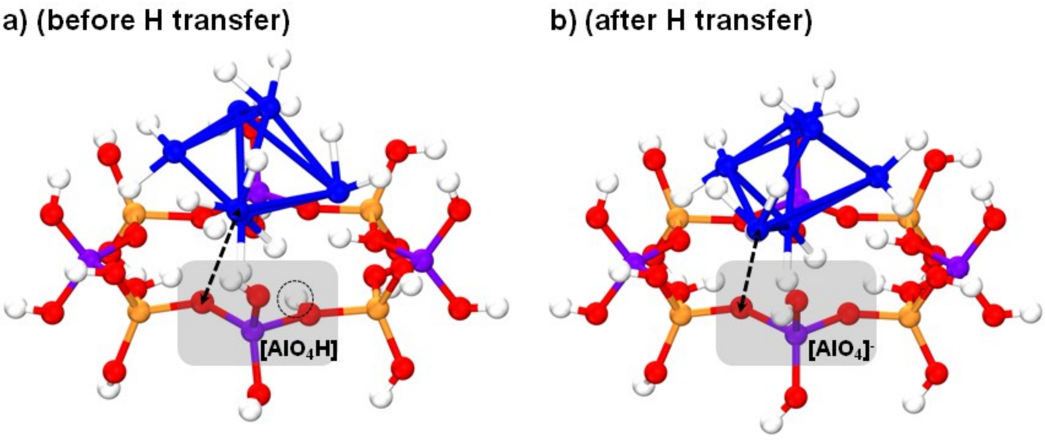

Fig. S3. DFT optimized structures before and after the proton rearrangement step between surface hydroxyl groups (OH) at the Pt-zeolite interface (R2 in Fig. S4b), yielding a H^+-deficient defect site of $[AlO_4]^-$ and a H^+-rich defect site of $[AlO_4H_2]^+$. Pt_6H_{12} nanoparticle developed a specific interaction with the $[AlO_4]^-$ site, where Pt-O distance is only 2.5 Å.

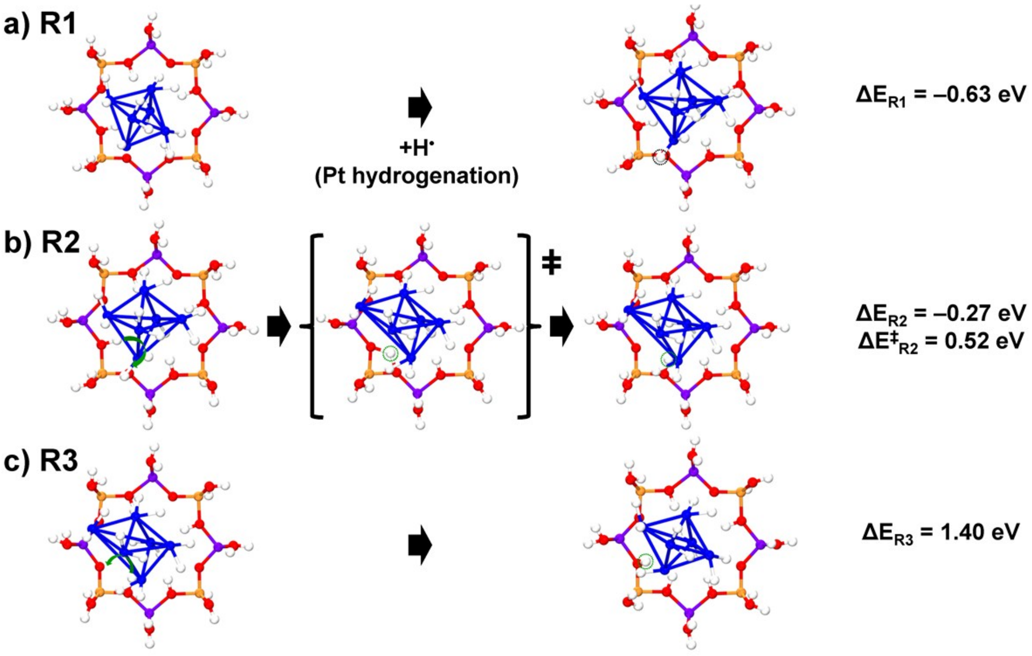

Fig. S4. DFT optimized structures and reaction energies during the H_2 activation and H spillover steps at the Pt-zeolite interface. (a) R1: hydrogenation step of Pt_6H_{11}, yielding Pt_6H_{12} (ΔE = –0.63 eV). (b) R2: proton rearrangement step between surface hydroxyl groups (OH), yielding a H^+-deficient defect site of $[AlO_4]^-$ and a H^+-rich defect site of $[AlO_4H_2]^+$. This step is favorable by –0.27 eV and requires activation energy of 0.52 eV. (c) R3: H spillover step. One H atom of the Pt_6H_{12} cluster transfers to the adjacent zeolite surface, yielding a surface OH. The Mulliken spin population of the spilt-over H is 0.00 (no radical character). This step requires reaction energy of 1.40 eV.

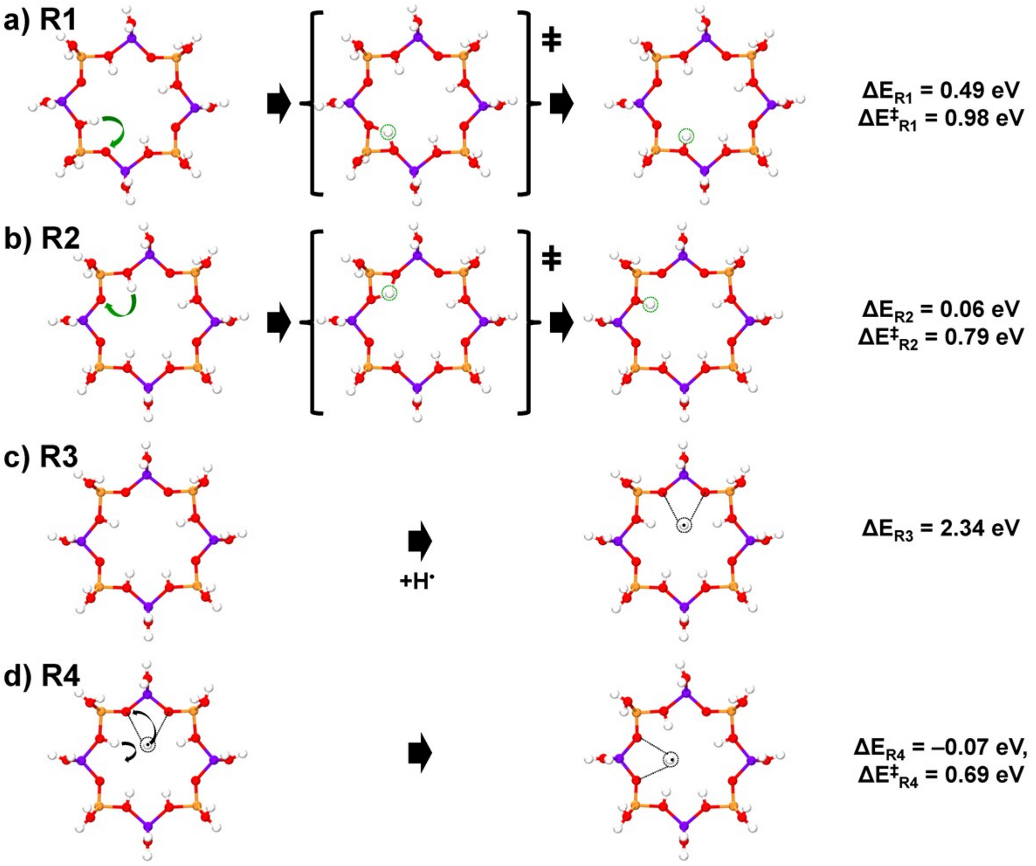

Fig. S5. DFT optimized structures and reaction energies during the H diffusion steps at the internal domain of a defect-free zeolite. (a) R1: proton rearrangement step between surface OH groups, yielding a H^+-deficient defect site of $[AlO_4]^-$ and a H^+-rich defect site of $[AlO_4H_2]^+$. This step requires reaction energy of 0.49 eV with activation energy of 0.98 eV. (b) R2: sequential proton rearrangement step. This step requires reaction energy of 0.06 eV with activation energy of 0.79 eV. (c) R3: spilt-over H migration step from the Pt-zeolite interface into the defect-free zeolite domain. This requires reaction energy of 2.34 eV. (d) R4: H radical migration step via bond exchange between the three-centered O-H-O bond and the adjacent O-H bond of the surface OH group. This step requires reaction energy of –0.07 eV with activation energy of 0.69 eV.

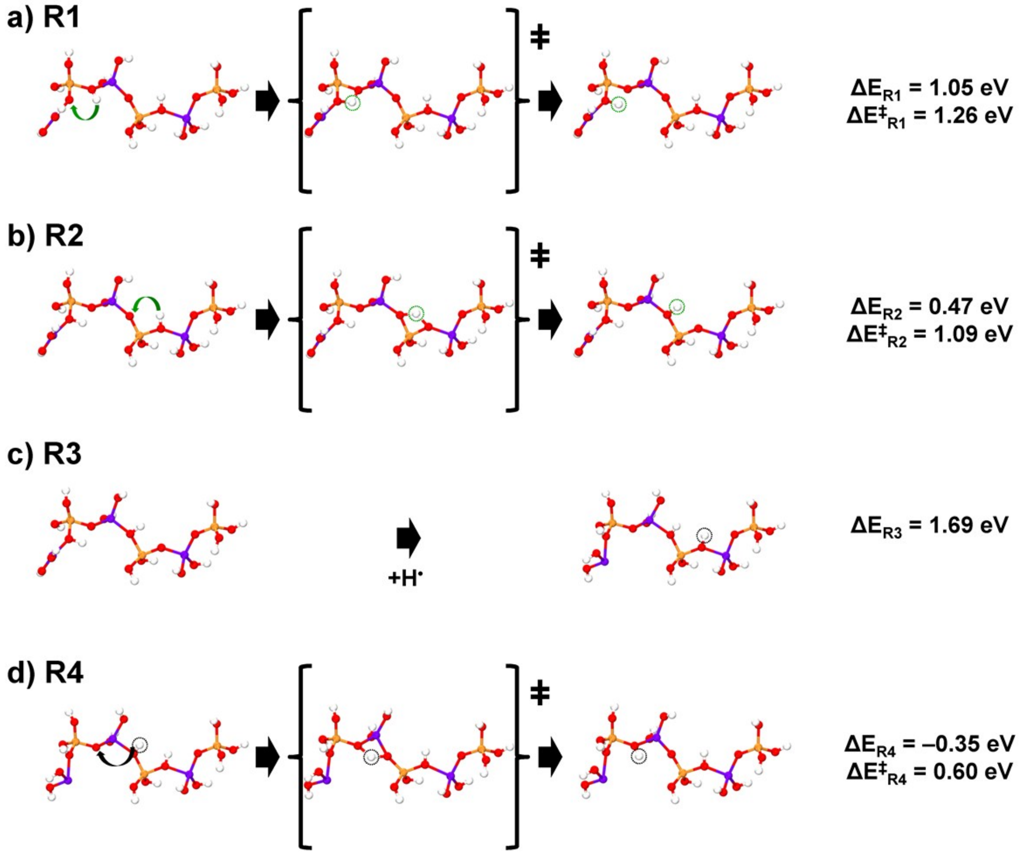

Fig. S6. DFT optimized structures and reaction energies during the H diffusion steps at the internal domain of a zeolite containing a Lewis acidic defect site (LAS). (a) R1: proton rearrangement step between surface OH groups, yielding a H^+-deficient defect site of $[AlO_4]^-$ and a H^+-rich defect site of $[AlO_3H]^+$. This step requires reaction energy of 1.05 eV with activation energy of 1.26 eV. (b) R2: sequential proton rearrangement step. This step requires reaction energy of 0.47 eV with activation energy of 1.09 eV. (c) R3: spilt-over H migration step from the Pt-zeolite interface. Here, e^- is localized in the LAS that is a good e^- accepting site, whereas H^+ is transferred to the H^+-deficient site, $[AlO_4]^-$, by forming a new surface OH. This requires reaction energy of 1.69 eV. (d) R4: proton migration step via surface proton hopping among surface OH groups. This step is an energetically favorable reaction with reaction energy of –0.35 eV and requires activation energy of 0.60 eV.

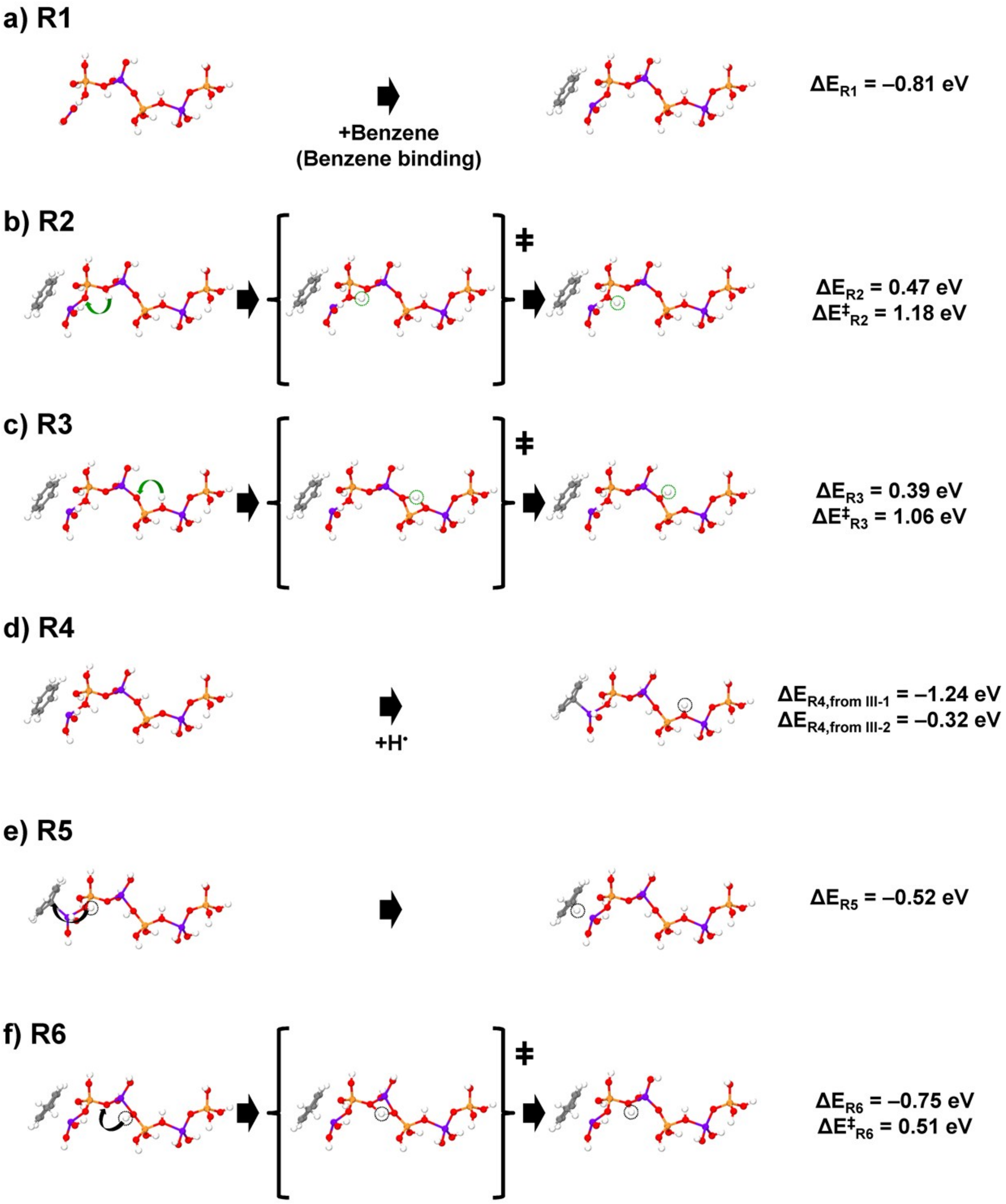

Fig. S7. DFT optimized structures and reaction energies during the H diffusion steps at the external domain of a zeolite with a Lewis acidic defect site (LAS). (a) R1: benzene adsorption step with binding energy of –0.81 eV. Benzene binds to the external tri-coordinated Al site. (b) R2: proton rearrangement step between surface OH groups, yielding a H^+-deficient defect site of $[AlO_4]^-$ and a

H^+-rich defect site of $[AlO_3H]^+$. This step requires reaction energy of 0.47 eV with activation energy of 1.18 eV. (c) R3: sequential proton rearrangement step. This step requires reaction energy of 0.39 eV with activation energy of 1.06 eV. (d) R4: spilt-over H migration step from the internal zeolite domain. This step has reaction energy of −1.24 eV or –0.32 eV for the case of migration from the defect-free zeolite domain or the case of migration from the zeolite domain with a LAS, respectively. (e) R5: benzene hydrogenation step with reaction energy of –0.52 eV, forming C_6H_7. (f) R6: another proton migration step to recover the initial state via surface proton hopping among surface OH groups. This step is an energetically favorable with reaction energy of –0.75 eV and requires activation energy of 0.51 eV.

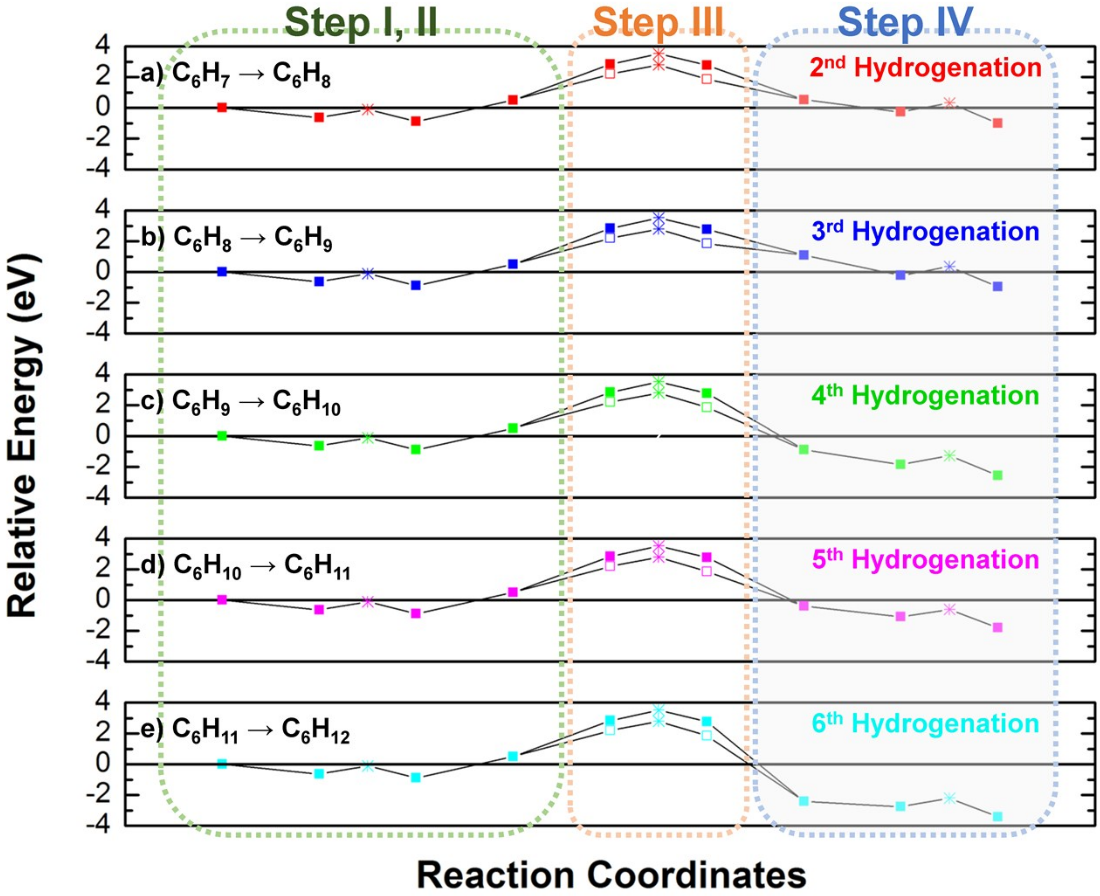

Fig. S8. Overall reaction energy diagrams for the sequential hydrogenations of unsaturated organic molecules, yielding (a) C_6H_8, (b) C_6H_9, (c) C_6H_{10}, (d) C_6H_{11}, and (e) C_6H_{12} (cyclohexane). Intermediate states and transition states are marked as squares and stars, respectively. Filled and empty squares in step III denote the energetics when the spilt-over H migrates over the defect-free regime and the LAS comprising regime in the zeolite surface, respectively.

Table S1. Estimated diffusion constant (*D*) and migration time (τ) for atomic hydrogen over the zeolite surface using the transition state theory as a function of the activation energy ($\Delta E_{act.}$).

$\Delta E_{act.}$ (eV)	D (Å^2/s)	τ (s/nm^2)
0.5	3.69×10^{9}	2.71×10^{-8}
0.7	4.37×10^{7}	2.29×10^{-6}
1.3	7.22×10^{1}	1.39×10^{0}
2.0	1.30×10^{-5}	7.71×10^{6}