Supplementary Information

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

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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 [AlO₄]⁻ and a H⁺-rich defect site of [AlO₄H₂]⁺. Pt₆H₁₂ nanoparticle developed a specific interaction with the [AlO₄]⁻ 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\(_6\)H\(_{11}\), yielding Pt\(_6\)H\(_{12}\) (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\(_4\)H\(_2\)]\(^+\). 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\(_6\)H\(_{12}\) 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 \([\text{AlO}_4]^-\) and a H\(^+\)-rich defect site of \([\text{AlO}_4\text{H}_2]^+\). 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 [AlO₄]⁻ and a H⁺-rich defect site of [AlO₃H]⁺. 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, [AlO₄]⁻, 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 [AlO₄]⁻ and a
H⁺-rich defect site of [AlO₃H]⁺. 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: split-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 C₆H₇. (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) C₆H₈, (b) C₆H₉, (c) C₆H₁₀, (d) C₆H₁₁, and (e) C₆H₁₂ (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 ($\tau$) for atomic hydrogen over the zeolite surface using the transition state theory as a function of the activation energy ($\Delta E_{\text{act}}$).

<table>
<thead>
<tr>
<th>$\Delta E_{\text{act}}$ (eV)</th>
<th>$D$ (Å$^2$/s)</th>
<th>$\tau$ (s/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>$3.69 \times 10^9$</td>
<td>$2.71 \times 10^{-8}$</td>
</tr>
<tr>
<td>0.7</td>
<td>$4.37 \times 10^7$</td>
<td>$2.29 \times 10^{-6}$</td>
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<tr>
<td>1.3</td>
<td>$7.22 \times 10^1$</td>
<td>$1.39 \times 10^9$</td>
</tr>
<tr>
<td>2.0</td>
<td>$1.30 \times 10^{-5}$</td>
<td>$7.71 \times 10^6$</td>
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