Supporting Information

Unprecedented Single Platform via Cross linking of Zeolite and MOFs

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EXPERIMENTAL SECTION

General. All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. In order to functionalize NaY zeolite with -COOH, all preparations and manipulations were performed under Ar atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a PANalytical Empyrean diffractometer at 45 kV and 40 mA for Cu Ka (λ = 1.54046 Å)
with a scan speed of 5° min⁻¹ and a step size of 0.02° in 2θ. Focused ion beam (FIB), field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) were measured with Helios 650 in Seoul National University, National Center for Inter – University Research Facilities and national nanofab center. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was recorded with a PerkinElmer Optima-4300 DV in Seoul National University, National Center for Inter – University Research Facilities. Thermogravimetric analysis (TGA) were performed under N₂(g) at a scan rate of 15 °C min⁻¹ up to 800 °C with Q50 model devices from TA Instruments. High resolution TEM (HRTEM) images were obtained with JEM-ARM 200F, 200 kV. In situ FT-IR was recorded in Nicolet TM50 FT-IR spectrometer with loading H₂ or D₂ gas. In-situ neutron powder diffraction (NPD) was measured with loading H₂ gas in NOVA instrument of Japan proton accelerator research complex (J-PARC).

**Surface modification of NaY zeolite with –COOH (NaY-COOH):** Prior to modify the surface of NaY zeolite with carboxylate group, the particle size of NaY zeolite decreased by ball milling with zirconia ball for 12 h. The 35 ml of (3-aminopropyl)triethoxysilan (APTES) and 15 g of succinic anhydride dissolved in 200 ml of anhydrous N,N-dimethylformamide (DMF) and then stirred at ambient temperature for 20 minutes. The solution was transferred into the 250 ml of shlenk tube including 5 g of ball milled NaY and stirred at room temperature for 24 h. The resulting powder washed with fresh ethanol for five times. The powder filtered and dried at 60 °C under the vacuum.

![Scheme S1. Surface modification of zeolite with carboxylate.](image)
Pt doping in NaY zeolite (Pt/NaY): In order to incorporate the Pt nanoparticles on zeolite, ion sputtering (Model: E-1030 ion sputter, Hitachi; Pt target: 0.3 mm O.D: 57 mm) method was utilized. In argon condition, 0.2 g of NaY zeolite was located in sample chamber and 30 mA current was applied to Pt target for 150 second under the 0.1 torr. This process was repeated for four times. The collected samples carried out annealing process at 150 °C under high vacuum for overnight. Finally, gray color powder was resulted, and followed by surface modification of Pt/NaY zeolite with -COOH as above mentioned procedure.

Synthesis of NaY@MOF-5: To synthesize NaY@MOF-5, a seed mediated growth method was applied. It is a general method to prepare core-shell structure materials. 0.125g of NaY-COOH as a seed, 0.67 g of Zn(NO$_3$)$_2$ and 0.125 g of terephthalic acid (H$_2$BDC) were dissolved in 20 ml of N-methyl-2-pyrrolidone(NMP). The mixture was located into the 20 ml of vials and kept at 105 °C for 12h in the oven. As a results, core-shell morphology crystals were formed (the white color of zeolite as a core and transparent MOF-5 as a shell crystal). The composite crystals were simply separated from the pure MOF-5 crystals by using 500 μm size sieve due to the crystal size difference. The composites washed with fresh N,N-dimethylformamide (DMF).

Synthesis of Pt/NaY@MOF-5 and Pt/NaY@MOF-177: To incorporate Pt/NaY in MOF-5, same procedure of NaY@MOF-5 was repeated using Pt/NaY-COOH. For Pt/NaY@MOF-177, 0.04 g of benzetricarboxylic acid (H$_3$BTB), 0.180 g of Zn(NO$_3$)$_2$, and 0.05 g of Pt/NaY-COOH was dissolved in 4 ml of N,N-diethylformamide (DEF). After 20 minutes sonication, the solution located in the oven at 100 °C for 24 h. As a result black crystals of Pt/NaY@MOF-5 were formed. The composite crystals were simply separated from the pure MOF-5 crystals by using 500 and 300 μm size sieve due to the crystal size difference. The composites washed with fresh N,N-dimethylformamide (DMF).

Sample preparation of field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) measurement for cross-sectional area of Pt/NaY@MOF-5
In order to investigate the homogeneous dispersion of zeolite materials, FE-SEM and EDX elemental mapping of cross sectional area for a composite crystal (Pt/NaY@MOF-5) were recorded. To retain the formation of a crystal, a composite crystal was located on the cover glass and coated with epoxy resin. Epoxy molding was carried out at 100 °C for 10 min. The sample covered with epoxy was grinded from the surface to center by SiC paper (240grit - 400grit - 800grit - 1200grit) and diamond lapping film (9um - 3um - 1um - 0.5um) to observe the cross section area of crystal.

**Low pressure gas sorption measurements:** The gas adsorption–desorption experiments were carried out by using an automated micro pore gas analyzer, ASAP-2020 (micrometrics). All gases used were of 99.999% purity. The N\textsubscript{2} sorption isotherms were measured at 77 K. The H\textsubscript{2} sorption isotherms were monitored at 77 K and 87 K at each equilibrium pressure by the static volumetric method. After the gas sorption measurement was finished, the weight of the sample was measured precisely. Surface area was determined from N\textsubscript{2} adsorption isotherm measured at 77 K by using the Brunauer-Emmett-Teller (BET) taking the data in the range \( P/P_0 = 0.02 – 0.06 \) for MOF-5, NaY@MOF-5, and Pt/NaY@MOF-5. Pore volume was determined by using the Horvath- Kawazoe (HK) method.

**Estimation of heats of adsorption \((Q_{st})\) for H\textsubscript{2}:** The heats of adsorption for H\textsubscript{2} of each materials was estimated by using H\textsubscript{2} sorption data measured at 77 K and 87 K. A virial-type expression was used [eq (1)], which is composed of parameters \(a_i\) and \(b_i\) that are independent of temperature.\textsuperscript{51,52} In eq (1), \( P \) is pressure (atm), \( N \) is the amount adsorbed H\textsubscript{2} gas (mg g\textsuperscript{-1}), \( T \) is temperature (K), and \( m \) and \( n \) represent the number of coefficients required to adequately describe the isotherms. An equation was fit using the R statistical software package.\textsuperscript{53}

\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]  

(1)

To calculate the values of the isosteric heat of H\textsubscript{2} adsorption, eq (2) was applied, where \( R \) is the universal gas constant.
\[ Q_{st} = -R \sum_{i=0}^{n} a_i N^i \] (2)

**In situ infrared spectroscopy measurement:** *In situ* Fourier transform infrared (FT-IR) spectra were obtained from a Nicolet TM50 FT-IR spectrometer with deuterium and hydrogen gas to investigate the hydrogenation mechanism in the composite materials, NaY@MOF-5 and Pt/NaY@MOF-5. Powder samples were installed into the sample cell under the Ar atmosphere. The first spectrum from the initial sample was obtained at 300 K and vacuum. After deuterium or hydrogen gas (D\(_2\) or H\(_2\), 15 bar) was induced in the sample at room temperature, the sample cell was heated up to 400 K. The samples under the H\(_2\) or D\(_2\) atmosphere were measured depending on the time to observe the change of spectra by H\(_2\) chemisorption. (0 min. 90 min. and 180 min)

**In-situ Neutron Powder Diffraction (NPD) Measurement:** In order to measure *in situ* neutron powder diffraction (NPD), two samples were prepared (MOF-5, and Pt/NaY@MOF-5). The MOF-5 and Pt/NaY@MOF-5 were loaded in sapphire sample cell (Inner diameter: 5.8 mm and height: 60 mm). The crystals were activated under the vacuum, heating and injection of H\(_2\). After increase temperature up to 400 K, H\(_2\) gas introduced in the MOF-5 and Pt/NaY@MOF-5 under 50 bar and retained for 2 h. In order to get rid of physisorbed H\(_2\), sample cell evacuation was carried out for 4 h and sequentially temperature was cool down up to 300 K. All NPD patterns were recorded under the vacuum state. Therefore the change of powder diffraction pattern derived from chemisorbed hydrogen atoms.

**References**


S3. The software package is available online at http://www.r-project.org.
Figure S1. High resolution transmission electron microscopy (HRTEM) images for Pt/NaY in the different scales.
**Figure S2.** Optical microscope crystal image for (a) MOF-5. (b) NaY@MOF-5. (c) Pt/NaY@MOF-5. b and c crystals were sorted by 500 μm size sieve. (d) MOF-177. (e) Pt/NaY@MOF-177. e crystals were sorted by 500 and 300 μm size sieve. (f) Comparison of MOF-177 (left) and Pt/NaY@MOF-177 crystal (right).
Figure S3. Powder X-ray diffraction (PXRD) pattern for (a) Pt/NaY@MOF-5, (b) NaY@MOF-5, (c) as-synthesized MOF-5, (d) Simulated XRD pattern from single crystal data of MOF-5, and (e) NaY-COOH obtained using Cu Kα1 radiation (λ = 1.54046 Å).
Figure S4. Powder X-ray diffraction (PXRD) pattern for (a) Pt/NaY@MOF-177, (b) Simulated XRD pattern from single crystal data of MOF-177, and (c) NaY-COOH obtained using Cu Kα1 radiation ($\lambda =$ 1.54046 Å).
Figure S5. Focused ion beam (FIB) and field emission scanning electron microscope (FE-SEM) image (a) Pt/NaY@MOF-5 after FIB (b) Magnified image of part of FIB (c) Elemental mapping (d) Energy dispersive X-ray spectroscopy (EDS) analysis.
Figure S6. FE-SEM and EDX mapping of selected area in Pt/NaY@MOF-5 cross-section.
Figure S7. Thermogravimetric analysis (TGA) of MOFs and their composite materials. (a) MOF-5, NaY, NaY@MOF-5 and Pt/NaY@MOF-5. (b) MOF-177, NaY, and Pt@NaY@MOF-177.
Figure S8. Fitting of H$_2$ adsorption isotherm of (a) MOF-5, (b) NaY@MOF-5 and (c) Pt/NaY@MOF-5 measure at 77 K (red) and 87 K (green) for calculation of heat of adsorption ($Q_{st}$) for H$_2$.

Figure S9. Fitting of H$_2$ adsorption isotherm of (a) MOF-177, (b) Pt/NaY@MOF-177 measure at 77 K (red) and 87 K (green) for calculation of heat of adsorption ($Q_{st}$) for H$_2$. 

Figure S10. Neutron powder diffraction measurement. (a) Experiment scheme and (b) Difference between B step and C stage of Pt/NaY@MOF-5 (top) or MOF-5 (bottom) neutron powder diffractograms. The colored space was originated from chemisorbed hydrogen.
Figure S11. *In situ* FT-IR spectra of Pt/NaY@MOF-5 after loading H$_2$ gas at 400 K.
Figure S12. \textit{In situ} FT-IR spectra of Pt/NaY after loading D$_2$ gas at 400 K.
Table S1. Comparison of N$_2$ and H$_2$ gas sorption properties of MOFs and composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N$_2^a$</th>
<th>S$_{BET}$</th>
<th>Pt/Zn ratio$^b$</th>
<th>Al/Zn ratio$^b$</th>
<th>$V_{pore}^c$</th>
<th>H$_2$</th>
<th>$Q_{st}$</th>
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<tr>
<td></td>
<td>/ccg$^{-1}$</td>
<td>/m$^2$g$^{-1}$</td>
<td>/ mol/mol</td>
<td>/ mol/mol</td>
<td>/ccg$^{-1}$</td>
<td>/wt%</td>
<td>/kJmol$^{-1}$</td>
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<td>MOF-5</td>
<td>892</td>
<td>3373</td>
<td>N/A</td>
<td>N/A</td>
<td>1.30</td>
<td>1.26$^a$</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.78$^d$</td>
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<tr>
<td>NaY@MOF-5</td>
<td>724</td>
<td>2727</td>
<td>N/A</td>
<td>0.13</td>
<td>1.05</td>
<td>0.87$^a$</td>
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<tr>
<td>NaY: 7.95 wt%$^e$</td>
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<td></td>
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<td></td>
<td>0.78$^d$</td>
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<tr>
<td>Pt/NaY@MOF-5</td>
<td>727</td>
<td>2714</td>
<td>1.12x10$^{-3}$</td>
<td>0.07</td>
<td>1.05</td>
<td>1.11$^a$</td>
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<tr>
<td>Pt/NaY: 8.75 wt%$^e$</td>
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<td></td>
<td></td>
<td>0.66$^d$</td>
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<tr>
<td>MOF-177</td>
<td>1237</td>
<td>4801</td>
<td>N/A</td>
<td>N/A</td>
<td>1.83</td>
<td>1.21$^a$</td>
<td>4.22</td>
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<td></td>
<td>0.64$^d$</td>
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<tr>
<td>Pt/NaY@MOF-177</td>
<td>952.9</td>
<td>3159</td>
<td>6.32x10$^{-2}$</td>
<td>0.15</td>
<td>1.20</td>
<td>1.01$^a$</td>
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<tr>
<td>Pt/NaY: 3.97 wt%$^e$</td>
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<td></td>
<td></td>
<td>0.61$^d$</td>
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$^a$77 K, 1 atm, $^b$Based on the ICP-AES data. $^c$Calculated by Horvath- Kawazoe (HK) method. $^d$87 K, 1 atm. $^e$Based on the TGA data.