Electronic Supplementary Information

Low-temperature fabrication of Cu(I) sites in zeolites by using a vapor-induced reduction strategy

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Experimental Section

Materials.

Cu(II)Y zeolite was prepared by ion exchange of NaY with 0.5 mol/L $Cu(NO_3)_2$ aqueous solution at 90 °C for 48 h. The amount of Cu(II) in the ion-exchange solution was equivalent to 5-fold cation-exchange capacity. After ion exchange, the zeolite suspension was filtered and the solid was washed thoroughly, followed by dried at 100 °C overnight.

The conversion of Cu(II)Y to Cu(I)Y was conducted by vapour-induced reduction (VIR). About 0.1 g Cu(II)Y was put in a open vial and kept inside an autoclave containing about 1 mL methanol (CH_3OH) with no direct contact between the solid and the solution. The autoclave was then heated at 220 °C for 6 h. After the autoclave rapidly cooled to the room temperature, the vial with powder was taken out quickly, vacuumized by a Schlenk line to remove residual CH_3OH, and kept in the inert atmosphere. The obtained sample was denoted as Cu(I)Y-V.

For the autoreduction (AR) method, 0.1 g Cu(II)Y was treated in an Ar flow at 450 °C for 6 h with a heating rate of 2 °C min^{-1}. The resultant sample was denoted as Cu(I)Y-A.

Characterization.

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation in the 2θ range from 5° to 60° at 40 kV and 40 mA. The N_2 adsorption-desorption isotherms were measured using an ASAP 2020 apparatus at −196 °C. Prior to analysis, the samples were evacuated at 200 °C for 4 h. The Brunauer-Emmett-Teller (BET) surface area was calculated at relative pressure ranging from 0.05 to 0.25. The total pore volume was derived from the amount adsorbed at a relative pressure of about 0.99. H_2-temperature programmed reduction (TPR) experiments were carried out on a BELSORP BEL-CAT-A apparatus. For Cu(I)Y-V, the sample were pressed into wafers, broken into small platelets (20-40 mesh) and pretreated at 150 °C under He for 3 h. After cooling to room temperature in the He atmosphere, the gas was switched to 10% H_2/He mixed gas (30 mL min^{-1}). The sample was heated to 1000 °C at a rate of 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Physical Electronic PHI-550 spectrometer equipped with an Al Kα X-ray source (hv=1486.6 eV) operating at 10 kV and 35 mA. The mechanism of reaction was processed in a temperature-programmed apparatus equipped with a mass spectrometer (MS). The temperature of the sample was raised linearly at rate of 2 ºC min^{-1} from room temperature up to 600 ºC. CH_3OH was introduced into the sample by the means of Ar bubbling.

Gas adsorption test.

Single component gases adsorption of propylene (C_3H_6) and propane (C_3H_8) were undertaken using an ASAP 2020 analyzer. The samples were degassed at 150 °C for 3 h before analysis, then the sample was back-filled with nitrogen and transferred to the analysis system. Free space was measured using helium (99.999%), assuming that the helium is not adsorbed at the studied temperature. Adsorption isotherms of C_3H_6 and C_3H_8 at 298 K were measured in a water bath.

The adsorption selectivity of propylene over propane on Cu(I)Y can be defined as $S_{ij}= (x_i/y_i)/(x_j/y_j)$, where x_i and x_j are the equilibrated adsorption capacities of components propylene and propane respectively, and y_i and y_j are the molar fractions of components of propylene and propane in gas phases respectively. For the pure propylene and propane adsorption, Dual-Site Langmuir mode (DL) model was chosen to fit their adsorption isotherms. Considering the ideal adsorption solution theory (IAST) can accurately describe gas-mixtures adsorption, the DL-IAST was employed to predict binary gas mixture adsorption on various materials.

Table S1. Structural properties, Cu content, and adsorption performances of samples.

Adsorbent	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	Cu content[a] (%)		Adsorbed amount[b] (mmol/g)	
			Cu(I)	Cu(II)	Propylene	Propane
NaY	726	0.35	−	−	3.67	3.16
Cu(II)Y	661	0.34	0	100	3.83	2.58
Cu(I)Y-A	624	0.32	41.5	58.5	4.12	2.54
Cu(I)Y-V	598	0.33	86.3	13.7	4.15	1.32

[a] Calculated from XPS results. [b] Measured at 298 K and 1 atm..

Table S2. Fitting parameters derived from isothermal data at 25 °C.

Adsorbent	Adsorbate	q_c (mmol/g)	q_i (mmol/g)	K_c (atm^{-1})	K_i (atm^{-1})	R^2
NaY	Propylene	1.0770	2.6040	14.6750	1562.9120	0.9992
	Propane	3.0456	2.8188	46.0693	0.0664	0.9998
Cu(II)Y	Propylene	1.1813	2.6983	7.5004	832.3938	0.9976
	Propane	2.5028	532.6053	29.0025	0.0003	0.9984
Cu(I)Y-A	Propylene	1.1190	3.0950	5.8120	1027.1330	0.9984
	Propane	2.4488	824.2950	25.1506	0.0002	0.9996
Cu(I)Y-V	Propylene	1.0361	3.1318	7.4378	930.1153	0.9982
	Propane	1.0674	1.3693	42.1972	0.2516	0.9998

Table S3. Adsorbed amount of propylene and propane for some adsorbents.

Adsorbent	Adsorbed amount (mmol/g)		Equilibrium Selectivity	Reference
	Propylene	Propane		
Cu(I)Y-V	4.15	1.32	3.14	This work
13X	2.6	2.2	1.18	[1]
Li-exchanged 13X	2.5	2.0	1.25	[2]
5A	2.5	2.0	1.25	[1]
Actived carbon	5.2	4.5	1.15	[1]
Silica gel	2.0	1.4	1.43	[3]
SBA-15	1.3	1.2	1.08	[4]
CuCl/NaX	1.9	1.4	1.36	[5]
CuCl/γ-Al_2O_3	0.7	0.2	3.50	[6]
SiAl20Cu5[a]	1.8	1.2	1.50	[7]
SiAl20Cu20[a]	0.9	0.6	1.50	[7]
$CuA_{10}B_1$[b]	1.6	0.9	1.78 (10.4)[c]	[8]
CuA_2B_1[b]	3.9	3.0	1.30 (2.7)[c]	[8]

[a] Cylindrically shaped aluminosilicates with a Si:Al molar ratio of 20 modified with copper loading of 5 % and 20 %; [b] Cu-functionalized porous organic polymer (POP) by adjusting the molar ratios of monomers 1,4-diethynyl-2,3-dihydroxybenzene (A) and Td-directing tetrakis (4-ethynyl) methane (B) with 10 : 1 and 2 : 1, respectively. [c] The values in parentheses are IAST selectivity.

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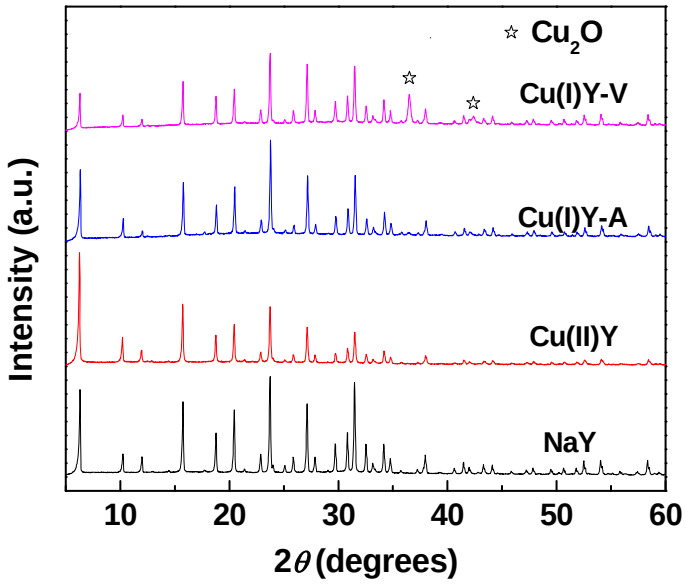

Figure S1. XRD patterns of NaY, Cu(II)Y, Cu(I)Y-A, and Cu(I)Y-V samples.

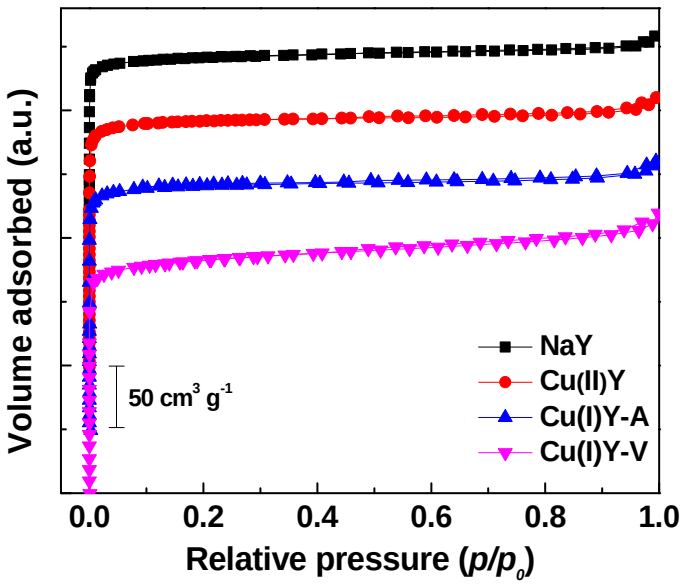

Figure S2. N_2 adsorption-desorption isotherms of NaY, Cu(II)Y, Cu(I)Y-A, and Cu(I)Y-V samples. Curves are plotted offset for clarity.

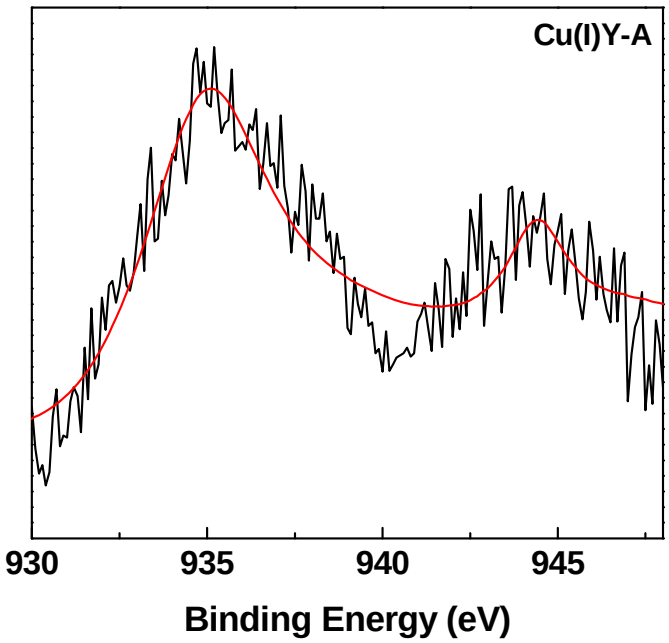

Figure S3. XPS spectra of Cu $2p_{3/2}$ for Cu(I)Y-A.

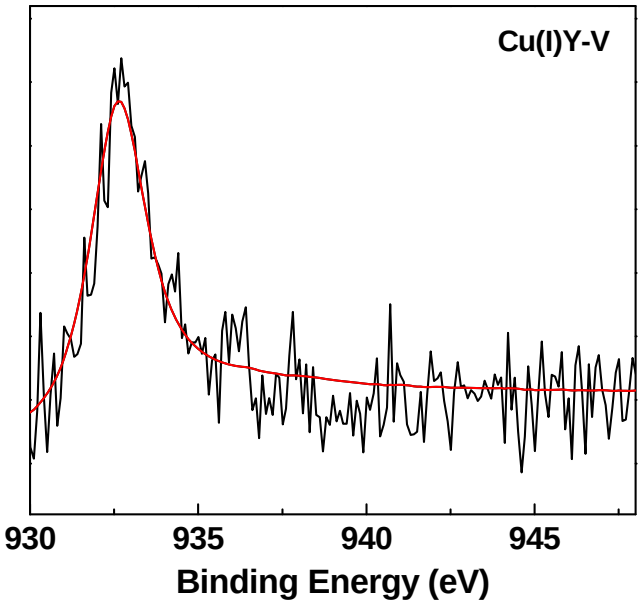

Figure S4. XPS spectra of Cu $2p_{3/2}$ for Cu(I)Y-V.

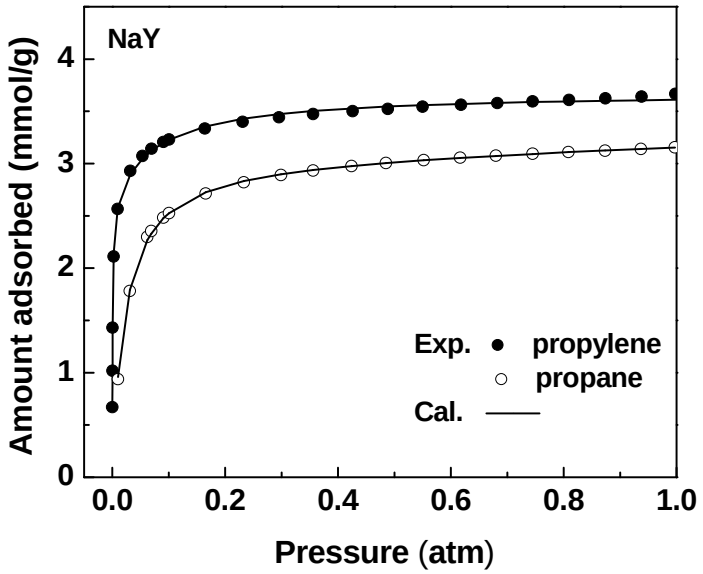

Figure S5. Adsorption isotherms of propylene and propane on NaY.

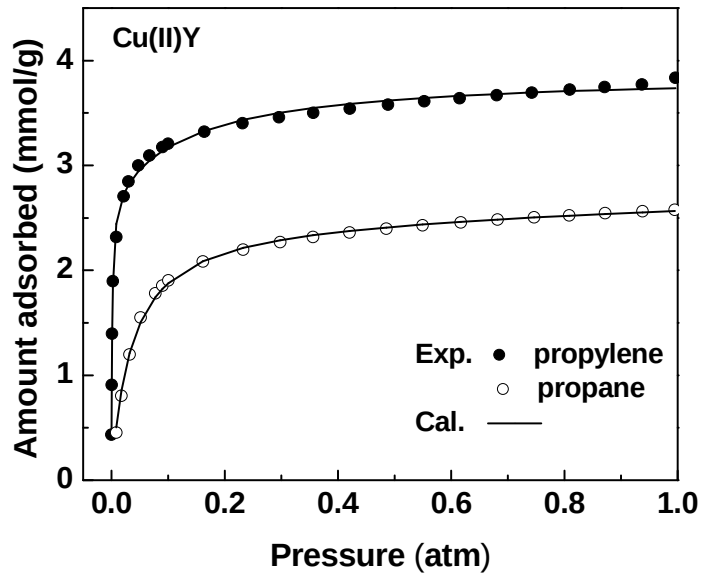

Figure S6. Adsorption isotherms of propylene and propane on Cu(II)Y.

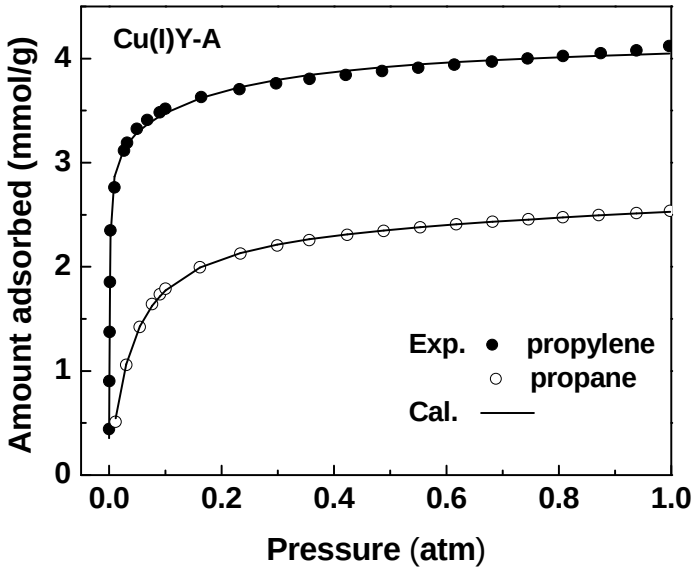

Figure S7. Adsorption isotherms of propylene and propane on Cu(I)Y-A.

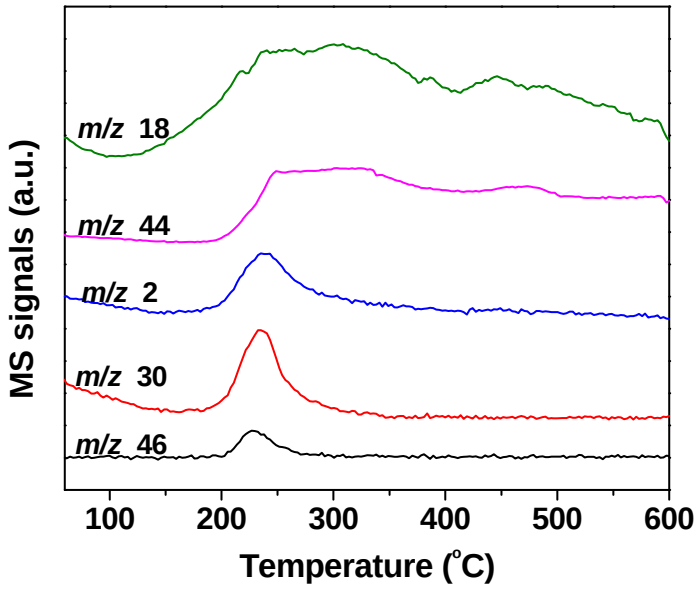

Figure S8. MS-monitored temperature programmed reaction of methanol vapor with Cu(II)Y.