Supplementary Material for PCCP

Electronic supplementary information

Existence of dual species composed of Cu^+ in CuMFI being bridged by C_2H_2

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Fig. S1

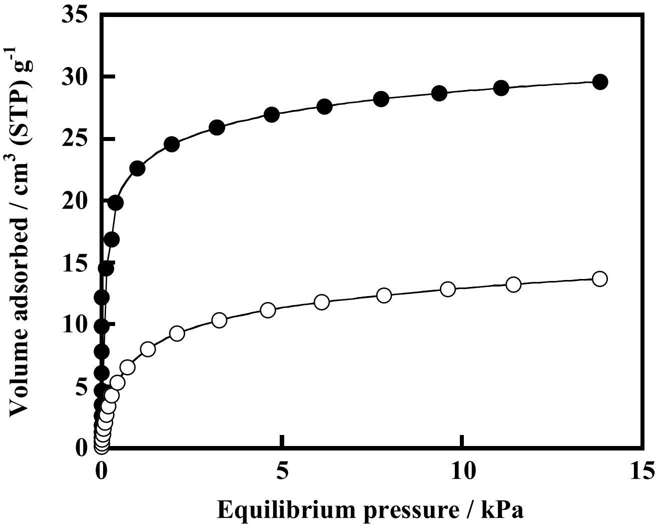

Fig. S1 Adsorption isotherms of CO at 298 K for CuMFI (copper-ion-exchange level: 130%). Filled and open symbols represent the first adsorption and second adsorptions, respectively.

For the CuMFI sample evacuated at 873 K for 4 h under a reduced pressure of 1.3 mPa, the first adsorption isotherm of CO was measured volumetrically at 298 K as with that of C_2H_2 (in text). After the first run, the sample was re-evacuated at 298 K for 4 h under a reduced pressure of 1.3 mPa, and then the adsorption isotherm was again measured at 298 K (second adsorption).

The CO molecule is well-known to be specifically adsorbed on monovalent copper ions (Cu^+).[1–3] Here, we intended to estimate the number of the Cu^+ ions formed in CuMFI through the evacuation at 873 K by utilizing CO as a probe molecule. Fig. S1 shows the first and second adsorption isotherms of CO on CuMFI measured at 298 K. In the lower CO-pressure regions, the amounts of the CO adsorbed on CuMFI for the first and second adsorptions increase remarkably; these isotherms are of Langmuir type, indicating a strong interaction of Cu^+ in CuMFI with CO. The monolayer capacities estimated by applying the Langmuir equation to the isotherms obtained were 29.08 and 13.84 cm^3 (STP: Standard Temperature and Pressure) g^{-1} for the first and second adsorptions, respectively. The difference in the adsorbed amounts between the first and second adsorptions was assumed to be the irreversibly adsorbed amount or the number of irreversible adsorption sites, *i.e.*, Cu^+. According to the same manner as done in our previous works,[4–6] the ratio of the total number of the Cu^+ ions to the total number of the copper ions in CuMFI, that is, the reduction rate of Cu^{2+} to Cu^+ ($N_{Cu+}/N_{Cu(total)}$), was evaluated from both the number of irreversibly adsorbed CO and the number of the copper ions contained in sample. The value of $N_{Cu+}/N_{Cu(total)}$ for the present CuMFI sample was 0.92. It was thus found that most of copper ions in CuMFI take the monovalent electronic state.

We estimated the ratio of the number of the adsorbed C_2H_2 or CO_2 molecules to the total number of Cu^+ ions in CuMFI, $n_{C2H2 \text{ or } CO2}/N_{Cu+}$ by assuming that the Cu^+ ions in the sample adsorb C_2H_2 or CO_2 at 298 K. Using both the numerical values of the storage capacities of C_2H_2 and CO_2 at an equilibrium pressure of 0.02 kPa (at the start of the linear part of the first isotherm after increasing the amount of adsorption steeply), respectively 16.82 and 0.66 $cm^3 g^{-1}$ and of $N_{Cu+}/N_{Cu(total)}$ (*i.e.*, 0.92) gave the n_{C2H2}/N_{Cu+} of 1.11 and the n_{CO2}/N_{Cu+} of 0.04.

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Fig. S2

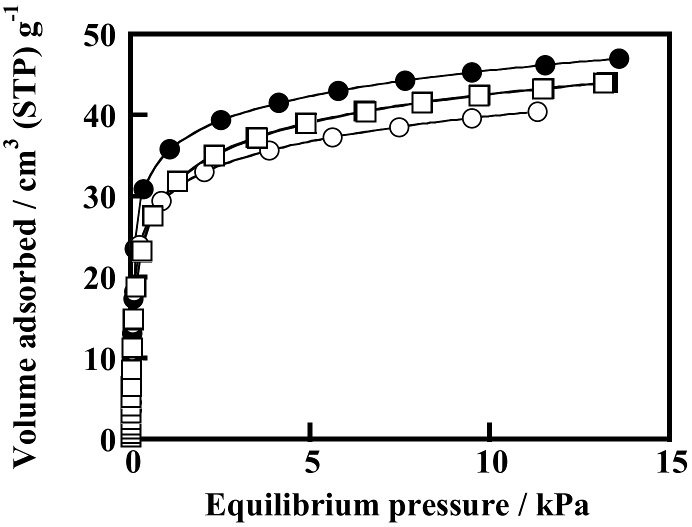

Fig. S2 Adsorption isotherms of C_2H_2 (circles) and CO_2 (squares) at 298 K for NaMFI. Filled and open symbols represent the first adsorption and second adsorptions.

Fig. S3

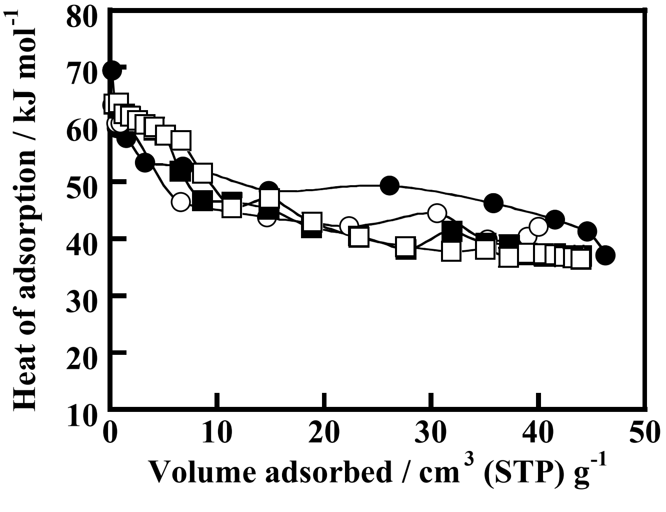

Fig. S3 Heats-of-adsorption curves of C_2H_2 (circles) and CO_2 (squares) at 298 K for NaMFI. Filled and open symbols represent the first adsorption and second adsorptions.

Fig. S4

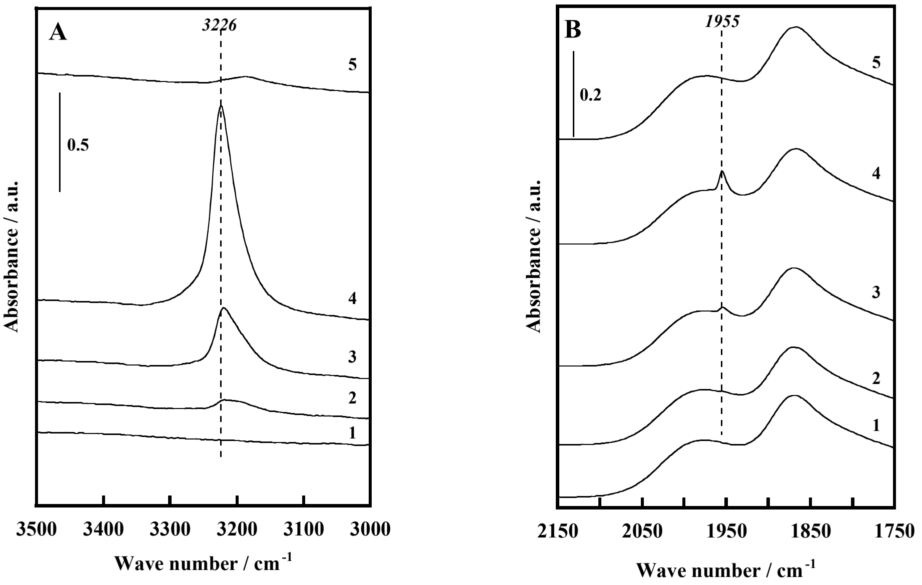

Fig. S4 IR spectra recorded in the ranges of (A) 3500–3000 and (B) 2150–1750 cm^{-1} for NaMFI treated in the following manner: (1) evacuation at 873 K; exposure to C_2H_2 gas at equilibrium pressures of (2) 1.33 ; (3) 7.98 Pa; and (4) 0.11 kPa. The spectrum 5 was measured at room temperature after re-evacuation at room temperature.

The IR spectra for NaMFI measured in the same manner as done for CuMFI are shown in Fig. S4. When exposing the NaMFI sample to C_2H_2 gas at room temperature, the sharp bands are clearly observed at 3226 and 1955 cm^{-1} (spectra 2–4). These bands are attributed to the respectively ν_3 C–H and ν_1 C≡C stretching vibration modes in the adsorbed C_2H_2 on Na^+.[1–3] As with the interaction of CuMFI with C_2H_2, from the positions of the C–H and C≡C IR absorption bands observed for NaMFI, the extents of the band-shift were evaluated to be 56 and 19 cm^{-1}, respectively. These values are considerably smaller than those for CuMFI, indicating that the interaction of Na^+ with C_2H_2 is relatively weak. The adsorbed C_2H_2 molecules were almost desorbed from NaMFI by the evacuation at room temperature (spectrum 5). The results obtained support the ones of the measurements of the first and second adsorption isotherms and heats-of-adsorption of C_2H_2 for NaMFI. Such the interaction of Na^+ with C_2H_2 was interpreted to be caused only by an electrostatic force.

References

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Fig. S5

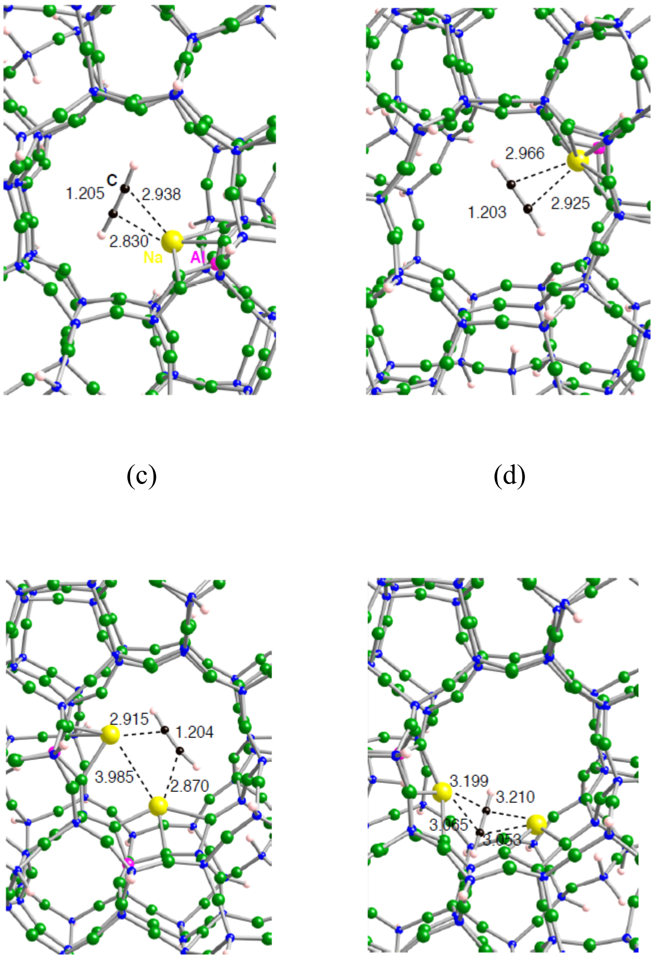
(a) (b) (c) (d)

Fig. S5 Four optimized structures of C_2H_2 adsorbed on NaMFI obtained at B3LYP level of theory. A Na–$AlSi_{91}O_{151}H_{66}$ cluster is used as a NaMFI model. Each bond length represents in Å. (a and b) The sodium cations locate above a 5-membered or 6-membered ring on a wall of a straight channel, respectively. The two sodium cations in c and d are in the second-nearest and third-nearest (Na–Na: 4.488 Å; C–C: 1.205 Å) positions, respectively. In the optimization, we used the 6-311G* basis set for the Na cations. Calculated vibrational frequencies of the adsorbed C_2H_2 molecules are given in Table S1. The monosodium model a can well reproduce C≡C stretching frequencies obtained experimentally. See Fig. S4.

Table S1 Calculated Frequency Shifts of the Adsorbed C_2H_2 on NaMFI (Δv_{cal}: cm^{-1})

	model a	model c	model d
Mode[a]	Δv_{cal}	Δv_{cal}	Δv_{cal}
v_1 (C≡C)	35.8	–26.8	–13.9
v_2 (C–H)	78.5	43.7	1.7
v_3 (C–H)	80.2	54.6	139.5

$\Delta v_{cal} = v_{cal}$ (C_2H_2 (g)) – v_{cal} (adsorbed C_2H_2)