

$E(\text{adsorbent}-\text{Cu}_n\text{-ZSM-5})$ is the total energy of an optimized structure for an adsorbent bound to $\text{Cu}_n\text{-ZSM-5}$, $E(\text{adsorbent})$ is that of an optimized structure for an adsorbent, and $E(\text{Cu}_n\text{-ZSM-5})$ is that of an optimized structure for $\text{Cu}_n\text{-ZSM-5}$. In the estimation, the $E_{\text{stabilization}}$ values were corrected for basis set superposition errors (BSSEs) by using the counterpoise method [36]. Within the B3LYP calculations, the optimized separations between a copper cation and a framework oxygen atom fall in the range of 1.89 to 2.55 Å, being consistent with the previous DFT results [37-44]. The ranges of the calculated Cu–O separations are in good agreement with those obtained from the XRD [45] and EXAFS [46-48] analyses (1.98~2.56 Å). Thus the theoretical method of our choice is appropriate for the present study.

3. Results and Discussion

3.1. ZSM-5 containing monocopper cation ($\text{Cu}_1\text{-ZSM-5}$)

3.1.1. The small monocopper zeolite model

First we investigate bindings of an unsaturated hydrocarbon into a monocopper cation bound to a small zeolite framework ($\text{AlSi}_2\text{O}_4\text{H}_8$) for obtaining a baseline for comparison. In the small zeolite model, the monocopper cation is coordinated by two framework oxygen atoms. Using the small zeolite model, we obtained optimized geometries for the binding of an unsaturated hydrocarbon into the monocopper cation, as shown in Figure 2.

Figure 2. (a) Optimized structures for the binding of an unsaturated hydrocarbon ((1) C_2H_2 or (2) C_2H_4) into the monocopper cation bound to the $\text{AlSi}_2\text{O}_4\text{H}_8$ model, and (b) their key orbital interactions.

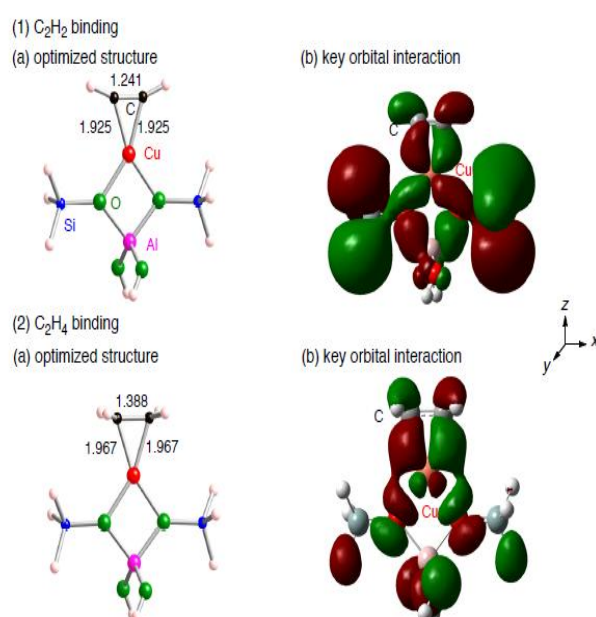


Figure 2 shows that the unsaturated hydrocarbons bind into the monocopper cation in a η^2 -bridging fashion. The Cu–C bond lengths were optimized to be 1.925 and 1.967 Å in the acetylene and

ethylene cases, respectively. The optimized structures lie 33 kcal/mol below their dissociation limits toward an unsaturated hydrocarbon and the small zeolite model. The $E_{\text{stabilization}}$ values are consistent with those reported in the previous theoretical studies [49-52]. The stabilization mainly comes from in-phase interactions between the $d_{xz}(\text{Cu})$ orbital of the extraframework monocopper and a π^* orbital of C_2H_2 or C_2H_4 , as shown in Figure 2. Due to the orbital interactions, the Cu(I) cation can donate electrons to the empty π^* orbital of an unsaturated hydrocarbon. Accordingly, their CC bonds are activated by the bindings: the optimized CC bond lengths in the acetylene (1.241 Å) and ethylene (1.388 Å) cases are longer than the unperturbed cases by 0.042 Å and 0.061 Å, respectively.

The adsorbed acetylene and ethylene cannot retain linear $D_{\infty h}$ and planar D_{2h} structures, respectively. The geometrical distortions change their vibrational structures. In fact, we see in Tables 1 and 2 that calculated CC stretching vibrational frequencies in the adsorbed acetylene and ethylene are 1793.8 and 1529.4 cm^{-1} , respectively [53]. The values are smaller than those of free acetylene and ethylene (2001.4 and 1645.2 cm^{-1} , respectively). The significant decrease in the CC stretching vibrational frequencies is due to the CC bond activation. Furthermore, their bindings into the extraframework copper cation make CC stretching modes infrared (IR)-active, due to symmetry lowering. Note that CC stretching vibrational modes of free C_2H_4 and C_2H_2 span A_g and Σ_g^+ , respectively and thus the modes are IR-inactive [54,55]. Similar symmetry lowering can be seen in the symmetric CH stretching mode in the adsorbed C_2H_2 , and thus a new IR peak appears around 3273 cm^{-1} after the C_2H_2 binding into the monocopper cation [56-58].

Table 1. Calculated vibrational frequencies (cm^{-1}) of CC and CH stretching modes of C_2H_2 before and after the binding into the small monocopper zeolite model.

	Free C_2H_2			C_2H_2 on Cu_1 -zeolite	
	Symmetry	Frequency	IR intensity ^a	Frequency	IR intensity ^a
C≡C stretch	Σ_g^+	2001.4	0.00	1793.8	1.12
C–H stretch	Σ_g^+	3400.0	0.00	3273.7	0.40
C–H stretch	Σ_u^+	3300.5	1	3204.0	1

^a IR intensities are given relative to that of the C–H stretching mode spanning Σ_u^+ .

Table 2. Calculated vibrational frequencies (cm^{-1}) of CC and CH stretching modes of C_2H_4 before and after the binding into the small monocopper zeolite model.

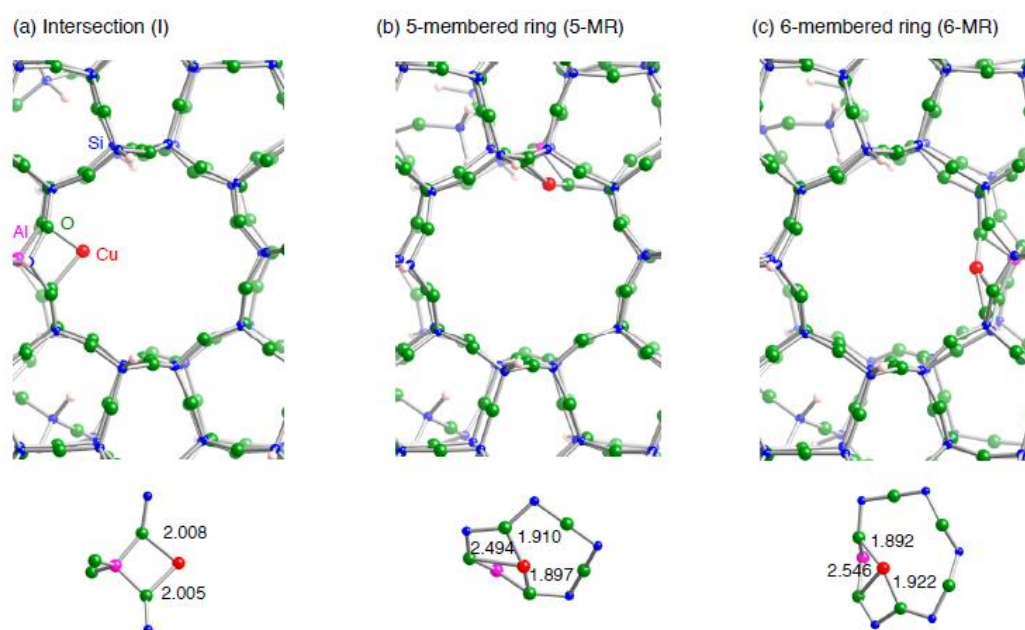
	Free C_2H_4			C_2H_4 on Cu_1 -zeolite	
	Symmetry	Frequency	IR intensity ^a	Frequency	IR intensity ^a
C≡C stretch	A_g	1645.2	0.00	1529.4	0.32
C–H stretch	A_g	3036.3	0.00	3023.9	0.00
C–H stretch	B_{3g}	3089.8	0.00	3090.7	0.00
C–H stretch	B_{1u}	3021.3	0.64	3017.7	0.98
C–H stretch	B_{2u}	3117.5	1	3113.2	1

^a IR intensities are given relative to that of the C–H stretching mode spanning B_{2u} .

3.1.2. Realistic Cu₁-ZSM-5 model

In the previous section (3.1.1), we discussed how an unsaturated hydrocarbon binds into a two-coordinated copper cation by using the small zeolite model. Although we obtained a baseline of the Cu–C bindings, the information is not sufficient to fully understand inner Cu–C interactions in real Cu–ZSM-5 framework due to the variety of the copper coordination environment. The coordination environment should change *d*-splittings of an extraframework copper cation, and therefore the *d*– π^* interactions are influenced by the copper sites. As a result, the coordination environment should determine the attraction forces operating between the copper cation and an unsaturated hydrocarbon.

Figure 3. Local structures of three optimized structures for a monocopper cation sitting inside the AlSi₉₁O₁₅₁H₆₆ ZSM-5 model. (a) the copper cation sits at the intersection between a straight and a zigzag channel, denoted by **I**. (b) the copper cation sits above a 5-membered ring of a wall along a straight channel, denoted by **5-MR**. (c) the copper cation sits above a 6-membered ring of a wall along a straight channel, denoted by **6-MR**.



ZSM-5 zeolite has 12 distinguishable tetrahedral(T)-sites in the orthogonal structure. Ref. [37] shows there is no significant difference between the relative energies of ZSM-5 where one Al atom replaces one Si atom in different T-sites. In addition, Nachtigall and Bell separately investigated CO adsorption into Cu–ZSM-5 with one substituted Al atom in different T-sites. Their extensive studies show that the interaction energies between CO and Cu–ZSM-5 as well as CO stretching frequencies change significantly, depending on Cu site types. Also they indicated that the location of the Al atom does not have influence on the binding energies. Judging from the interaction energies, binding sites for an extraframework cation inside ZSM-5 are categorized into three subgroups in Figure 3: one is a cation site near an intersection between a straight and a sinusoidal channels, denoted by **I**, and the others are cations located above a 5-membered and 6-membered rings of a wall along a straight channel, denoted by **5-MR** and **6-MR**, respectively. Along their theoretical findings, we considered

the three binding sites for the Cu cation inside ZSM-5, where the substituted Al atom is located near the cation.

Figure 3 shows that the copper coordination environment in the **I** configuration is similar to that in the small zeolite model: in the **I** configuration, the monocopper cation is bound to two framework oxygen atoms near the substituted Al atom. In contrast, the **5-MR** and **6-MR** configurations have the monocopper cations with a coordination number of 3 [16]. Due to the different copper coordination environment, their electronic configurations are different, as shown in Table 3. The coordination of a Cu(I) cation into ZSM-5 framework results in some degree of the $3d^{10} \rightarrow 3d^9 4s^1$ promotion [41]. In terms of the $3d^{10} \rightarrow 3d^9 4s^1$ promotion, there is a slight difference between the **I** and **5-MR** (**6-MR**) configurations: the amount of the 4s electron in the **I** configuration (0.25e) is less significant than those in the **5-MR** and **6-MR** configurations (~0.4 e). Since we found the differences in the Cu coordination environments in the three configurations, it is interesting to investigate how the copper coordination environment affects the interactions with an unsaturated hydrocarbon.

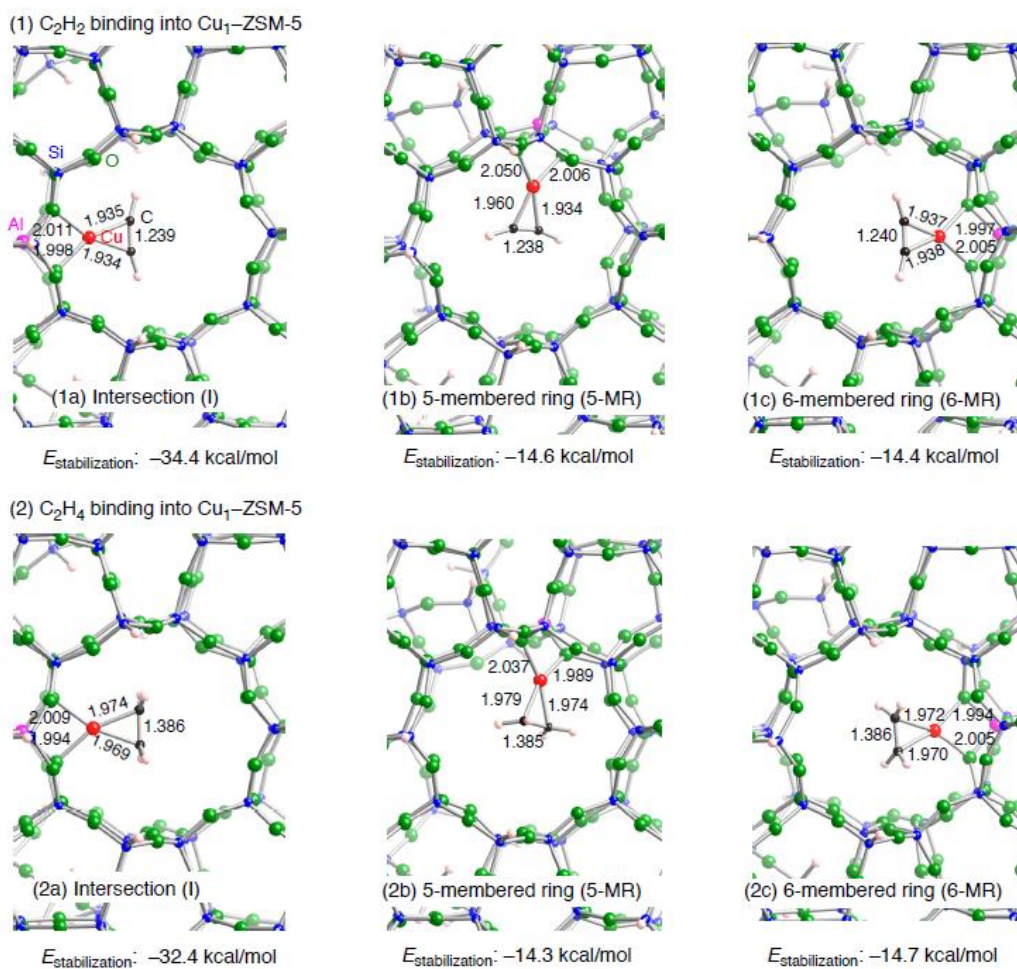
Table 3. Electronic configurations of Cu–ZSM-5 before and after the binding of an unsaturated hydrocarbon, based on natural atomic orbital analyses (NPA).

Configuration	Adsorbent	Electronic configuration
I	–	4s (0.25) 3d (9.84)
	C ₂ H ₂	4s (0.36) 3d (9.56) 4p (0.01)
	C ₂ H ₄	4s (0.37) 3d (9.57) 4p (0.01)
5-MR	–	4s (0.42) 3d (9.73)
	C ₂ H ₂	4s (0.36) 3d (9.57) 4p (0.01)
	C ₂ H ₄	4s (0.36) 3d (9.58) 4p (0.01)
6-MR	–	4s (0.44) 3d (9.71)
	C ₂ H ₂	4s (0.36) 3d (9.55) 4p (0.01)
	C ₂ H ₄	4s (0.37) 3d (9.57) 4p (0.01)

Optimized structures for unsaturated hydrocarbons adsorbed on a Cu₁–ZSM-5 model are shown in Figure 4. Table 4 tabulates key parameters for all optimized geometries. We can see in Figure 4 the same types of bindings of the unsaturated hydrocarbons into the copper cation (η^2 -fashion), irrespective of different copper coordination environment as well as types of unsaturated hydrocarbon considered. Similar binding fashions have been already reported in Refs. [49–52]. In the η^2 -fashion of the C₂H₂ (C₂H₄) bindings, the optimized Cu–C and CC bond lengths are ~1.94 (~1.97) Å and ~1.24 (~1.38) Å, respectively. The CC bonds in the adsorbed unsaturated hydrocarbons are lengthened relative to the free unsaturated hydrocarbons, indicating that the Cu–C bond formation results in the CC bond activation. Interestingly the Cu–C bondings in the η^2 -fashion are completely identical to those of the small model. Note that the copper coordination environments in the three configurations are also same after the bindings, in contrast to those before the bindings. Reflecting the same Cu coordination environments, the three models have similar electron configurations of the Cu(I) cation in Table 3. In addition, the amounts of electron transferring (~0.2e) upon the bindings are similar among the three configurations. However, we see slight difference between the **I** and **5-MR** (**6-MR**) configurations in terms of how the electrons transfer between an unsaturated hydrocarbon and Cu–ZSM-5. In the **I** configuration, the 4s electron densities increase, whereas the 3d

electron densities decrease. Since the two Cu–O bond lengths remain almost unchanged during the binding (Figures 3 and 4), the electron transfer is responsible for the Cu–C bond formation. On the other hand, we can see that both $3d$ and $4s$ orbitals are depopulated upon the bindings in the **5-MR** and **6-MR** configurations. Compared with the **I** configuration, the electron transfers in these configurations originate from not only the formation of the two Cu–O bonds but also significant changes in the copper coordination environments. In fact we see in Figures 3 and 4 that the Cu coordination number changes from 3 to 2, upon the bindings of an unsaturated hydrocarbon into an extraframework copper at **5-MR** or **6-MR** configuration. In contrast, such changes in the Cu coordination number are not seen in the **I** configuration.

Figure 4. Local structures of three optimized structures for the binding of an unsaturated hydrocarbon ((1) C_2H_2 or (2) C_2H_4) into a monocopper cation embedded inside the $AlSi_91O_{151}H_{66}$ ZSM-5 model. (a) the copper cation sits at the intersection between a straight and a zigzag channel, denoted by **I**. (b) the copper cation sits above a 5-membered ring of a wall along a straight channel, denoted by **5-MR**. (c) the copper cation sits above a 6-membered ring of a wall along a straight channel, denoted by **6-MR**. Optimized bond lengths are in Å. The $E_{\text{stabilization}}$ values are in kcal/mol.



Despite the same binding types in the three configurations, the stabilization energies depend on their copper coordination environment: the calculated $E_{\text{stabilization}}$ values in the **I** configuration (−34.4 (C₂H₂) and −32.4 (C₂H₄) kcal/mol) are more pronounced than those in the **5-MR** configuration (−14.6 (C₂H₂) and −14.3 (C₂H₄) kcal/mol) and the **6-MR** configuration (−14.4 (C₂H₂) and −14.7 (C₂H₄) kcal/mol). The stabilization energies in the **I** configuration are almost the same as those in the small zeolite models, whereas those in the **5-MR** and **6-MR** configurations are different. The different $E_{\text{stabilization}}$ values are also associated with the changes in the copper coordination environments upon the bindings. Here we consider quantitatively why the copper coordination environment plays an essential role in determining the stabilization energies. In general, an extraframework cation shifts from its original position by approaching of an adsorbent to the cation. The cation shifts destabilize a zeolite structure itself. The destabilization by the cation shifts counteracts direct attractive interactions between an extraframework cation and an adsorbent. Thus the balance between the destabilization by the cation shifts and the stabilization by the direct interactions determines a stable conformation of an adsorbent inside a zeolite. The importance of the balance has been already discussed by Nachtigall and coworkers [59,60]. We can see dependences of the destabilization on the copper coordination environment in Table 4, where the destabilization energies $E(\text{deform})$ are listed. The $E(\text{deform})$ values are defined by $E(\text{deformed Cu-ZSM-5}) - E(\text{adsorbent-free Cu-ZSM-5})$. Here $E(\text{deformed Cu-ZSM-5})$ is the single-point-energy of a deformed Cu-ZSM-5 taken from an optimized adsorbent-Cu-ZSM-5 complex, and $E(\text{adsorbent-free Cu-ZSM-5})$ is the total energy of an optimized adsorbent-free Cu-ZSM-5 structure. Positive $E(\text{deform})$ values indicate that a Cu-ZSM-5 itself is destabilized by the inner coordination bond formation. Table 4 indicates strong site-dependencies of the $E(\text{deform})$ values.

Table 4. Key parameters of the optimized structures for an unsaturated hydrocarbon adsorbed on a dicopper active center embedded inside a realistic ZSM-5 model.

Configuration ^a	Adsorbent	Binding mode	Cu-C ^b	CC ^b	$E_{\text{stabilization}}$ ^c	$E(\text{deform})$ ^d
I	C ₂ H ₂	η^2	1.934, 1.935	1.239	−34.4	2.6
5MR	C ₂ H ₂	η^2	1.934, 1.960	1.238	−14.6	20.4
6MR	C ₂ H ₂	η^2	1.937, 1.938	1.240	−14.4	22.5
I	C ₂ H ₄	η^2	1.969, 1.974	1.386	−32.4	2.3
5MR	C ₂ H ₄	η^2	1.974, 1.979	1.385	−14.3	17.8
6MR	C ₂ H ₄	η^2	1.970, 1.972	1.386	−14.7	20.3

^a Configuration: I is the intersection site, 5MR and 6MR are the 5- and 6-membered sites.; ^b Bond lengths in Å.; ^c $E_{\text{stabilization}}$ in kcal/mol.; ^d $E(\text{deform})$ in kcal/mol.

In fact the $E(\text{deform})$ values in the **I** configuration (2.6 (C₂H₂) and 2.3 (C₂H₄) kcal/mol) are negligible relative to those in the **5-MR** configuration (20.4 (C₂H₂) and 17.8 (C₂H₄) kcal/mol) and the **6-MR** configuration (22.5 (C₂H₂) and 20.3 (C₂H₄) kcal/mol). The site-dependent $E(\text{deform})$ values are reasonable, because decreasing the copper coordination number in the **5-MR** and **6-MR** configurations loses attractive Cu–O interactions at some extent. Taking the different $E(\text{deform})$ values into account, we can understand that bindings of an unsaturated hydrocarbon to the monocopper cation in the **I** configurations are energetically favorable over those in the **5-MR** and **6-MR** configurations. Note that

the deformation energies are more significant than those in the interaction with NO molecule (the $E(\text{deform})$ values are 1 and 8 kcal/mol for intersection and channel wall sites, respectively [41]). The larger $E(\text{deform})$ values suggest that the η^2 -bindings require larger displacement of copper cations rather than the η^1 -bindings. In this situation we demonstrated from DFT calculations that the copper coordination environment is a key factor determining the bindings of an unsaturated hydrocarbon into an extraframework monocopper cation of ZSM-5.

3.2. ZSM-5 containing dicopper active center (Cu_2 -ZSM-5)

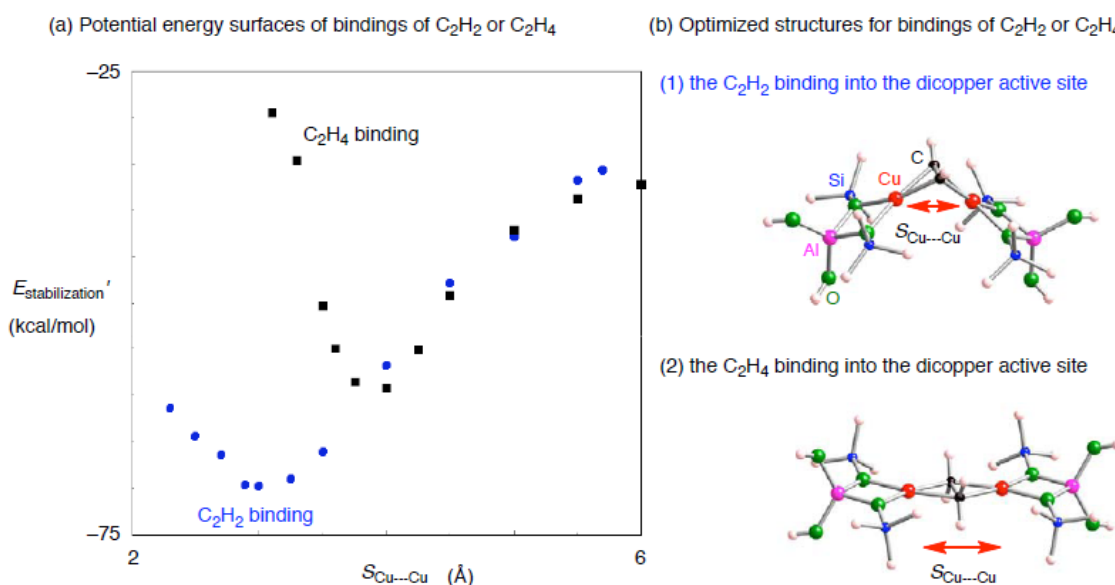
In this section we will focus on an unsaturated hydrocarbon bound to a dicopper active center embedded in ZSM-5. In this situation, configurations of the two copper cations within a ZSM-5 cavity may be responsible for the unsaturated hydrocarbon bindings, in addition to their copper coordination environment. Experimentally the presence of Cu pairs in ZSM-5 was demonstrated by using extended X-ray absorption fine structure (EXAFS) [61-63] spectroscopy and X-ray power diffraction [45] studies. To fully understand behaviors of an unsaturated hydrocarbon inside a ZSM-5 cavity, it is indispensable to clarify how configurations of the two copper cations inside ZSM-5 affect the properties of adsorbed unsaturated hydrocarbons.

3.2.1. The small dicopper zeolite model

First we use a small zeolite model containing the dicopper active center ($[\text{Cu}-\text{AlSi}_2\text{O}_4\text{H}_8]_2$) to increase our preliminary understanding of the interactions with an unsaturated hydrocarbon. Using the small dicopper zeolite model, we optimized an unsaturated hydrocarbon adsorbed on the dicopper active center, except for the $\text{Cu}\cdots\text{Cu}$ separation ($S_{\text{Cu}\cdots\text{Cu}}$). Potential energy surfaces of the approaching of an unsaturated hydrocarbon into the dicopper active center are seen in Figure 5 as a function of $S_{\text{Cu}\cdots\text{Cu}}$. Figure 5 shows their stabilization energies $E_{\text{stabilization}}$ defined as $-E(\text{adsorbent}) - E(\text{Cu}_2\text{-zeolite}[S_{\text{Cu}\cdots\text{Cu}}]) + E(\text{adsorbent-Cu}_2\text{-zeolite}[S_{\text{Cu}\cdots\text{Cu}}])$, where $E(\text{adsorbent})$ is the total energy of the optimized structure for an adsorbent, $E(\text{adsorbent-Cu}_2\text{-zeolite}[S_{\text{Cu}\cdots\text{Cu}}])$ is that of an optimized structure for an adsorbent bound to the small dicopper zeolite at a certain $S_{\text{Cu}\cdots\text{Cu}}$ value, and $E(\text{Cu}_2\text{-zeolite}[S_{\text{Cu}\cdots\text{Cu}}])$ is that of a Cu_2 -zeolite taken from the optimized $\text{adsorbent-Cu}_2\text{-zeolite}[S_{\text{Cu}\cdots\text{Cu}}]$ structure. When $S_{\text{Cu}\cdots\text{Cu}}$ is 6 Å, C_2H_2 or C_2H_4 binds into one copper cation bound to the $\text{AlSi}_2\text{O}_4\text{H}_8$ zeolite model. Then the optimized structures for the C_2H_2 and C_2H_4 bindings are, respectively, 35.6 and 37.2 kcal/mol stable relative to those in the dissociation limits toward an unsaturated hydrocarbon and the free small zeolite model with the two copper cations apart by 6 Å. Of course, the $E_{\text{stabilization}}$ values are close to those obtained in the small monocopper zeolite.

Decreasing the $\text{Cu}\cdots\text{Cu}$ separation, two Cu-C bonds are newly generated. As a result, an unsaturated hydrocarbon binds into both copper cations in a $\mu\text{-}\eta^2$: η^2 fashion. Because of the new Cu-C bond formation, the $E_{\text{stabilization}}$ values lower significantly until a certain $S_{\text{Cu}\cdots\text{Cu}}$ value. In fact we see in Figure 5 that the potential energy surface of the C_2H_2 -dicopper (C_2H_4 -dicopper) complex has one local minimum at $S_{\text{Cu}\cdots\text{Cu}}$ of 2.888 (3.735) Å.

Figure 5. (a) Potential energy surfaces of approaching of an unsaturated hydrocarbon (C_2H_2 or C_2H_4) into the smaller dicopper zeolite model ($[Cu-Al_1Si_3O_4H_8]_2$). $E_{\text{stabilization}}$ is plotted as a function of the $Cu\cdots Cu$ separation. (b) optimized structures for the binding of an unsaturated hydrocarbon ((1) C_2H_2 or (2) C_2H_4) into the small dicopper zeolite model.



As shown in Figure 5 and Table 5 the optimized C_2H_2 - and C_2H_4 -dicopper complexes lie, respectively, 34.0 and 21.4 kcal/mol below the structures with the $S_{Cu\cdots Cu}$ values of ~ 6 Å. These DFT results clearly show that the interactions of acetylene with the dicopper active center are more significant than the ethylene case. The differences between the acetylene and ethylene additions are unique in the dicopper cases, which cannot be seen in the monocopper cases. Moreover, we can see some discrepancy in the optimized structures between the acetylene and ethylene cases: the optimized C_2H_2 - Cu_2 -zeolite contains a $\mu-\eta^2:\eta^2$ Cu_2C_2 core with a butterfly form, whereas the C_2H_4 - Cu_2 -zeolite contains a planar $\mu-\eta^2:\eta^2$ core. Reflecting the structural differences, the C_2H_2 - Cu_2 -zeolite has a smaller $S_{Cu\cdots Cu}$ value than that in C_2H_4 - Cu_2 -zeolite.

Table 5. Key parameters of the optimized structures of an unsaturated hydrocarbon adsorbed onto a dicopper active center bound to a small zeolite model.

Adsorbent	Binding mode	Cu–C ^a	CC ^a	$S_{Cu\cdots Cu}$ ^b	$E_{\text{stabilization}}$ ^c
C_2H_2	$\mu-\eta^2:\eta^2$	1.932, 1.933	1.297	2.888	−69.6
		1.933, 1.934			
C_2H_4	$\mu-\eta^2:\eta^2$	2.003, 2.003,	1.449	3.735	−58.6
		2.003, 2.003			

^a Bond lengths in Å.; ^b $S_{Cu\cdots Cu}$ is the $Cu\cdots Cu$ separation in Å.; ^c $E_{\text{stabilization}}$ in kcal/mol.

Whether the Cu_2C_2 core has a planar or a butterfly structure can be confirmed by their IR spectra, especially their CC stretching vibrational modes (Tables 6 and 7). We see in Tables 6 and 7 that CC stretching vibrational frequencies were calculated to be 1557.1 and 1469.4 cm^{-1} in C_2H_2 and C_2H_4 adsorbed on the dicopper active center, respectively. Lower CC stretching frequencies than those in

the monocopper model are ascribed to more significant CC bond activation by the dicopper active center: the optimized CC bond lengths in the acetylene and ethylene additions are 1.297 and 1.449 Å, respectively (see Table 5). More importantly, the CC stretching vibrational mode in the acetylene addition is IR-active, whereas that in the ethylene addition is IR-inactive due to the planarity of its Cu₂C₂ core. The calculated IR data will help to determine how an unsaturated hydrocarbon binds into a dicopper active center embedded inside ZSM-5.

Table 6. Calculated vibrational frequencies (cm⁻¹) of CC and CH stretching modes of C₂H₂ before and after the binding into the small dicopper zeolite model.

	Free C ₂ H ₂			C ₂ H ₂ on Cu ₂ -zeolite	
	Symmetry	Frequency	IR intensity ^a	Frequency	IR intensity ^a
C≡C stretch	Σ _g ⁺	2001.4	0.00	1557.1	1.44
C–H stretch	Σ _g ⁺	3400.0	0.00	3170.0	0.90
C–H stretch	Σ _u ⁺	3300.5	1	3127.8	1

^a IR intensities are given relative to that of the C–H stretching mode spanning Σ_u⁺.

Table 7. Calculated vibrational frequencies (cm⁻¹) of CC and CH stretching modes of C₂H₄ before and after the binding into the small dicopper zeolite model.

	Free C ₂ H ₄			C ₂ H ₄ on Cu ₂ -zeolite	
	Symmetry	Frequency	IR intensity ^a	Frequency	IR intensity ^a
C≡C stretch	A _g	1645.2	0.00	1469.4	0.00
C–H stretch	A _g	3036.3	0.00	3004.9	0.00
C–H stretch	B _{3g}	3089.8	0.00	3085.4	0.00
C–H stretch	B _{1u}	3021.3	0.64	3001.8	17.10
C–H stretch	B _{2u}	3117.5	1	3100.5	1

^a IR intensities are given relative to that of the C–H stretching mode spanning B_{2u}.

3.2.2. Realistic Cu₂–ZSM-5 model

In section 3.2.1, we used the small dicopper zeolite model, and found differences between the dicopper and monocopper cations in terms of the interactions with an unsaturated hydrocarbon. Next we turn to dicopper active centers located in a 10-MR cavity of the realistic ZSM-5 model Al₂Si₉₀O₁₅₁H₆₀. Since copper cations usually sit near the Al substituted positions, the locations of the double Si → Al substitution within the ZSM-5 framework control the configurations of a dicopper active center. Here we consider four locations of the double substitution in Figure 6: the **2NN**, **3NN**, **4NN**, and **5NN** configurations contain the Al pairs being, respectively second, third, fourth, and fifth nearest-neighbors with respect to tetrahedral sites contained in the 10-MR. Using the different configurations of the Al pair, their initial geometries were constructed by placing each Cu apart by ~2.0 Å from two oxygen atoms bound to a substituted Al atom. After the B3LYP optimization, four configurations of the dicopper center inside ZSM-5 were obtained, as shown in Figure 6. The Cu•••Cu separation in Cu₂–ZSM-5 decreases in the order **5NN** (6.442 Å) > **4NN** (6.370 Å) > **3NN** (2.561 Å) > **2NN** (2.372 Å). The Cu•••Cu separations in the **2NN** and **3NN** configurations are close to those

obtained by EXAFS analyses (2.47–3.13 Å). In the optimized Cu₂–ZSM-5 structures, each Cu cation coordinates into two or three framework oxygen atoms. The Cu•••Cu separations are out of the range of a suitable span between the two copper cations into which an unsaturated hydrocarbon preferentially binds in a $\mu\text{-}\eta^2\text{:}\eta^2$ -fashion (Figure 5). Note that the formation of Cu pairs in the **3NN** and **2NN** configurations is consistent with the Spuhler's findings [38] by means of a combined quantum mechanics/interatomic potential function technique (QM-pot).

Taking varying Cu•••Cu separations by locations of the double Si → Al substitution into account, we discuss how an unsaturated hydrocarbon binds into a dicopper active center. Figure 7 shows the optimized structures for an unsaturated hydrocarbon adsorbed on a dicopper active center embedded in a ZSM-5 model, whose key parameters are listed in Table 8. We can see in Figure 7 and Table 8 two types of binding of C₂H₂ into a dicopper active center. In the **2NN** configuration, C₂H₂ binds into the dicopper active center in a $\mu\text{-}\eta^1\text{:}\eta^1$ fashion, whereas the **3NN**, **4NN**, and **5NN** configurations have a $\mu\text{-}\eta^2\text{:}\eta^2$ Cu₂C₂ core. In the **3NN**, **4NN**, and **5NN** configurations, the Cu•••Cu separations were optimized to be 3.047, 3.236, and 3.315 Å, respectively. These *S*_{Cu•••Cu} values are close to the separation between the two copper cations into which C₂H₂ binds in a $\mu\text{-}\eta^2\text{:}\eta^2$ fashion in Figure 5. The significant differences in the *S*_{Cu•••Cu} values between before and after the C₂H₂ binding ($\Delta S_{\text{Cu}\cdots\text{Cu}}$) indicate that two copper cations significantly shift after the binding. In contrast, the **2NN** configuration does not have a room, and thus the two copper cations cannot move to positions suitable for the C₂H₂ binding in a $\mu\text{-}\eta^2\text{:}\eta^2$ fashion. Instead, the **2NN** configuration adopts the $\mu\text{-}\eta^1\text{:}\eta^1$ binding fashion with a stabilization energy of −33.7 kcal/mol. Surprisingly the *E*_{stabilization} value is comparable to that of the **3NN** configuration (−35.8 kcal/mol), despite the different C₂H₂ binding fashions.

Figure 6. Local structures of four optimized Cu₂–ZSM-5 structures where the ZSM-5 framework was modeled as a Al₂Si₉₀O₁₅₁H₆₆ cluster. The four types of optimized structures can be distinguished by positions of double Si → Al substitution: the two substituted Al atoms within a ten-membered ring are second nearest neighbor (**2NN**), third nearest neighbor (**3NN**), fourth nearest neighbor (**4NN**), and fifth nearest neighbor (**5NN**). Optimized bond lengths are given in Å.

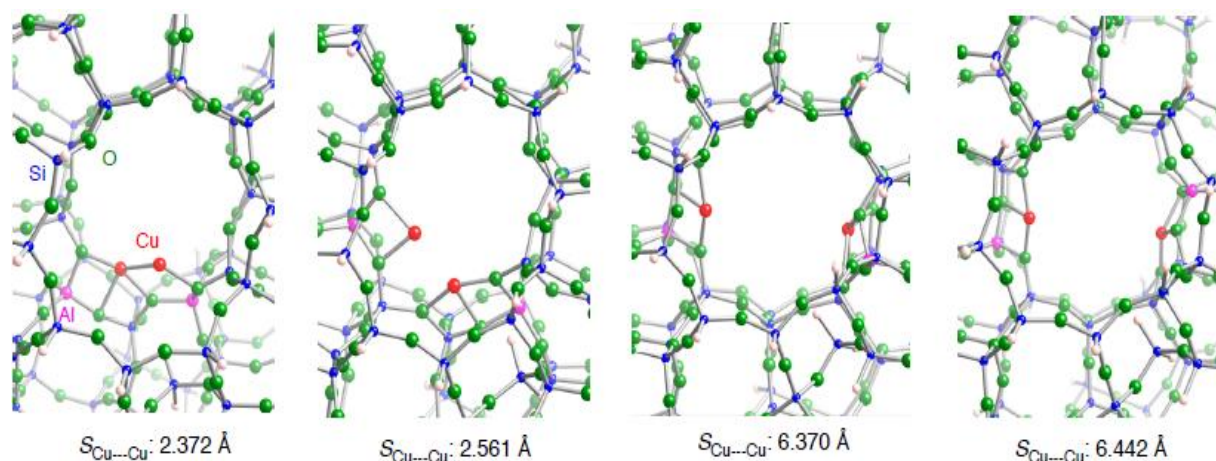
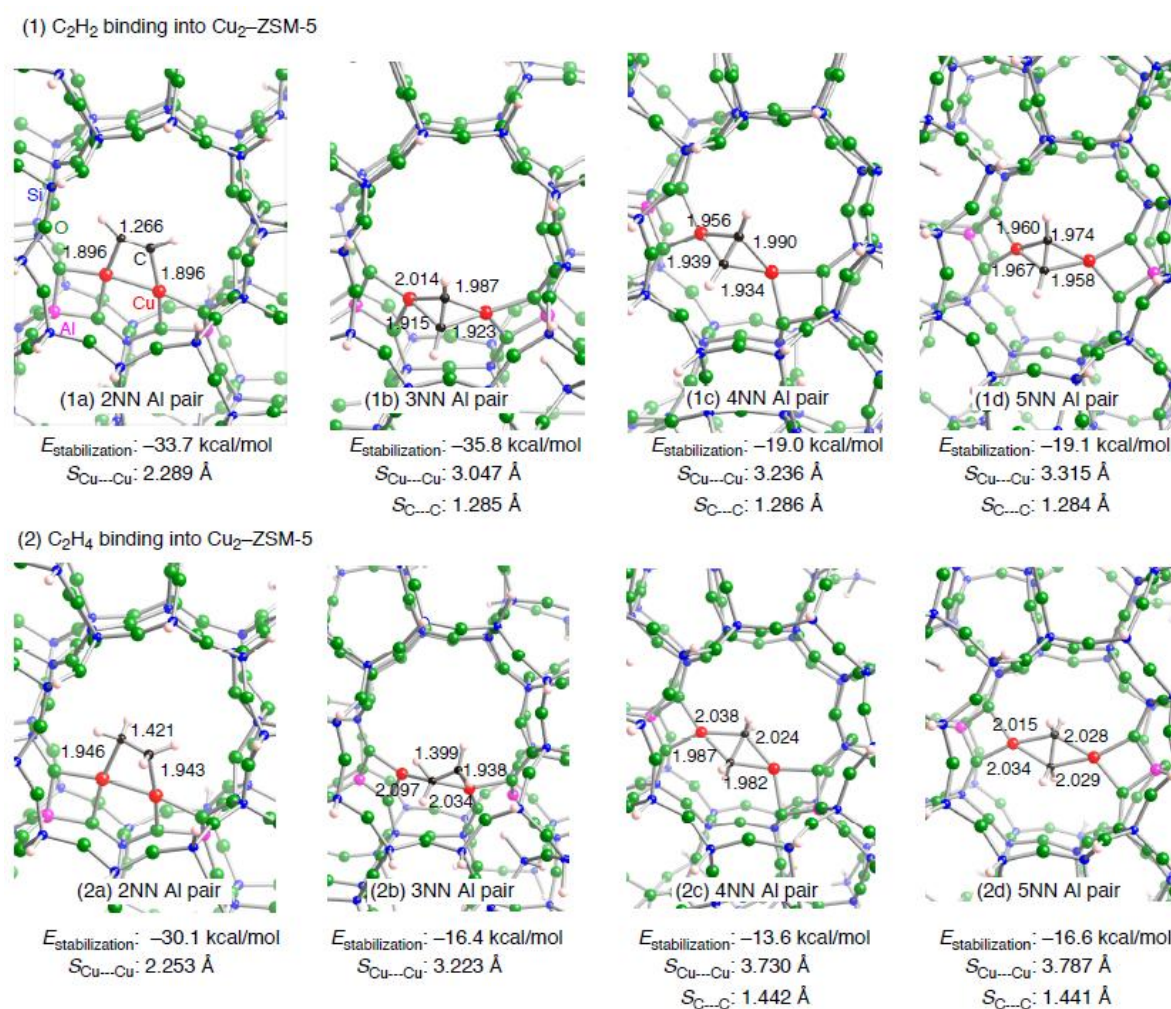


Figure 7. Local structures of four optimized structures for the binding of an unsaturated hydrocarbon ((1) C_2H_2 or (2) C_2H_4) into a dicopper active center embedded inside the $Al_2Si_{90}O_{151}H_{66}$ ZSM-5 model. The four types of optimized structure can be distinguished by positions of double Si \rightarrow Al substitution: the two substituted Al atoms within a ten-membered ring are (a) second nearest neighbor (2NN), (b) third nearest neighbor (3NN), (c) fourth nearest neighbor (4NN), and fifth nearest neighbor (5NN). Optimized bond lengths together with the $Cu\cdots Cu$ separations are given in Å. The $E_{stabilization}$ values are in kcal/mol.



In the above discussion, we found that whether the two copper cations smoothly shift determines a preferable C_2H_2 binding fashion in a ZSM-5 cavity. Although the importance of the copper shifts can be also seen in the monocopper case, the $E(\text{deform})$ values in the dicopper cases (Table 8) are more pronounced than those in the monocopper cases. In addition, we found from Table 8 strong dependences of the $E(\text{deform})$ values on the dicopper configurations: the $E(\text{deform})$ values decrease in the following order: $5NN \approx 4NN > 3NN > 2NN$. The decrease in the $E(\text{deform})$ values has a close relation to the $\Delta S_{Cu\cdots Cu}$ values. Table 8 shows that the $\Delta S_{Cu\cdots Cu}$ values decrease in the order $4NN \approx 5NN > 3NN > 2NN$, suggesting that the C_2H_2 bindings in the 5NN and 4NN configurations cause two copper cations to shift significantly, compared with those in the 3NN and 2NN

configurations. Therefore, the dependent $E(\text{deform})$ values are understandable. Reflecting the $E(\text{deform})$ values, the stabilization in the **4NN** and **5NN** configurations is less significant than that in the **3NN** configuration, because the destabilization by the cation shifts diminishes the attraction by the direct interactions. Thus the variety of the Cu–C bonding characters is unique in the restricted environment of ZSM-5.

Table 8. Key parameters of the optimized structures of an unsaturated hydrocarbon adsorbed onto a dicopper active center embedded inside a realistic ZSM-5 model.

Configuration ^a	Adsorbent	Binding mode	Cu–C ^b	CC ^b	$S_{\text{Cu}\cdots\text{Cu}}$ ^c ($\Delta S_{\text{Cu}\cdots\text{Cu}}$ ^d)	$E_{\text{stabilization}}$ ^e	$E(\text{deform})$ ^f
2NN	C ₂ H ₂	$\mu-\eta^1: \eta^1$	1.896, 1.896	1.266	2.289 (−0.083)	−33.7	19.0
3NN	C ₂ H ₂	$\mu-\eta^2: \eta^2$	1.915, 1.923, 1.987, 2.014	1.285	3.047 (0.486)	−35.8	24.7
4NN	C ₂ H ₂	$\mu-\eta^2: \eta^2$	1.934, 1.939, 1.956, 1.990	1.286	3.236 (−3.134)	−19.0	45.7
5NN	C ₂ H ₂	$\mu-\eta^2: \eta^2$	1.958, 1.960, 1.967, 1.974	1.284	3.315 (−3.127)	−19.1	47.2
2NN	C ₂ H ₄	$\mu-\eta^1: \eta^1$	1.946, 1.943	1.421	2.253 (−0.119)	−30.1	18.0
3NN	C ₂ H ₄	$\mu-\eta^1: \eta^2$	1.938, 2.034, 2.097	1.399	3.223 (0.662)	−16.4	25.5
4NN	C ₂ H ₄	$\mu-\eta^2: \eta^2$	1.982, 1.987, 2.024, 2.038	1.442	3.730 (−2.640)	−13.6	41.9
5NN	C ₂ H ₄	$\mu-\eta^2: \eta^2$	2.015, 2.028, 2.029, 2.034	1.441	3.787 (−2.655)	−16.6	43.1

^a Configuration: The **2NN**, **3NN**, and **4NN** configurations have Al pairs being second-, third-, and fourth nearest neighbors within a ten-membered ring of the ZSM-5 model, respectively.; ^b Bond lengths in Å.; ^c $S_{\text{Cu}\cdots\text{Cu}}$ is the Cu•••Cu separation in Å.; ^d $\Delta S_{\text{Cu}\cdots\text{Cu}}$ is the difference in the Cu•••Cu separation between before and after the binding of an unsaturate hydrocarbon.; ^e $E_{\text{stabilization}}$ in kcal/mol.; ^f $E(\text{deform})$ in kcal/mol.

Compared with the C₂H₂ bindings, more complicated binding modes are found in the C₂H₄ bindings into a dicopper center in Figure 7: the **2NN** configuration has a $\mu-\eta^1: \eta^1$ form, the **3NN** configuration has a $\mu-\eta^1: \eta^2$ form, and the **4NN** and **5NN** configurations have a $\mu-\eta^2: \eta^2$ form. The calculated $E_{\text{stabilization}}$ values are close to those obtained experimentally (−15.4 and −21.4 kcal/mol) [64]. The $\mu-\eta^2: \eta^2$ binding fashions in the **4NN** and **5NN** configurations are similar to that obtained in the small zeolite model: in both cases, the Cu and C atoms virtually lie in a plane. The Cu•••Cu separations in the **4NN** and **5NN** configurations (3.730 and 3.787 Å, respectively) are essentially identical to the equilibrium separation between C₂H₄ and the small zeolite model (3.735 Å in Figure 5), and thus the similarity in the binding fashion is reasonable. In contrast, the optimized $S_{\text{Cu}\cdots\text{Cu}}$ values in the **2NN** and **3NN** configurations are 1.482 and 0.512 Å smaller than the equilibrium

separation in the small dicopper zeolite model. Accordingly these configurations cannot adopt a $\mu\text{-}\eta^2\text{:}\eta^2$ binding fashion. Note that the $\mu\text{-}\eta^1\text{:}\eta^2$ binding fashion (**3NN**) is an intermediate between the $\mu\text{-}\eta^1\text{:}\eta^1$ (**2NN**) and $\mu\text{-}\eta^2\text{:}\eta^2$ (**4NN** and **5NN**) fashions. How C_2H_4 binds into a dicopper active center inside ZSM-5 is also followed by the balance rule. As shown in Table 8, destabilization of the $\text{Cu}_2\text{-ZSM-5}$ by the C_2H_4 binding is similar to that by the C_2H_2 binding from a viewpoint of energetics. However, direct interactions by the C_2H_4 binding are 11.0 kcal/mol weaker than those by the C_2H_2 binding (see Table 5). Compared with the C_2H_2 bindings, the importance of the destabilization by the cation shifts to determine a preferable C_2H_4 binding fashion is more effective rather than the direct attractive $\text{C}_2\text{H}_4\text{-dicopper}$ interactions.

4. Conclusions

We found from large-scale DFT calculations that characters of copper-carbon bonds formed inside ZSM-5 change significantly, depending on its copper coordination environment. Actually attractive interactions of an unsaturated hydrocarbon with a two-coordinated extraframework copper cation are significant relative those with a higher-coordinated copper cation. The dependences of the interactions are related with shifts of a copper cation accompanied by the bindings: the shift of a cation with a higher coordination number costs energy a lot. Thus site-preferences of two-coordinated copper cations as the unsaturated-hydrocarbon binding site are reasonable. When an unsaturated hydrocarbon binds into an embedded dicopper active center, configurations of the two copper cations are important to determine the bindings, in addition to its coordination environment. Because of the different interactions between an unsaturated hydrocarbon and a mono- or dicopper copper active center, various binding fashions (η^2 , $\mu\text{-}\eta^1\text{:}\eta^1$, $\mu\text{-}\eta^1\text{:}\eta^2$, and $\mu\text{-}\eta^2\text{:}\eta^2$ fashions) are expected in Cu-ZSM-5 . The variety of characters of the copper-carbon bonds is unique in the restricted environment of a zeolite.

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