









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  $\pi^*$  orbital of  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_4$ , as shown in Figure 2. Due to the orbital interactions, the Cu(I) cation can donate electrons to the empty  $\pi^*$  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  $\text{cm}^{-1}$ , respectively [53]. The values are smaller than those of free acetylene and ethylene (2001.4 and 1645.2  $\text{cm}^{-1}$ , 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  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  span  $A_g$  and  $\Sigma_g^+$ , 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  $\text{C}_2\text{H}_2$ , and thus a new IR peak appears around 3273  $\text{cm}^{-1}$  after the  $\text{C}_2\text{H}_2$  binding into the monocopper cation [56-58].

**Table 1.** Calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of CC and CH stretching modes of  $\text{C}_2\text{H}_2$  before and after the binding into the small monocopper zeolite model.

	Free $\text{C}_2\text{H}_2$			$\text{C}_2\text{H}_2$ on $\text{Cu}_1$ -zeolite	
	Symmetry	Frequency	IR intensity <sup>a</sup>	Frequency	IR intensity <sup>a</sup>
C≡C stretch	$\Sigma_g^+$	2001.4	0.00	1793.8	1.12
C–H stretch	$\Sigma_g^+$	3400.0	0.00	3273.7	0.40
C–H stretch	$\Sigma_u^+$	3300.5	1	3204.0	1

<sup>a</sup> IR intensities are given relative to that of the C–H stretching mode spanning  $\Sigma_u^+$ .

**Table 2.** Calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of CC and CH stretching modes of  $\text{C}_2\text{H}_4$  before and after the binding into the small monocopper zeolite model.

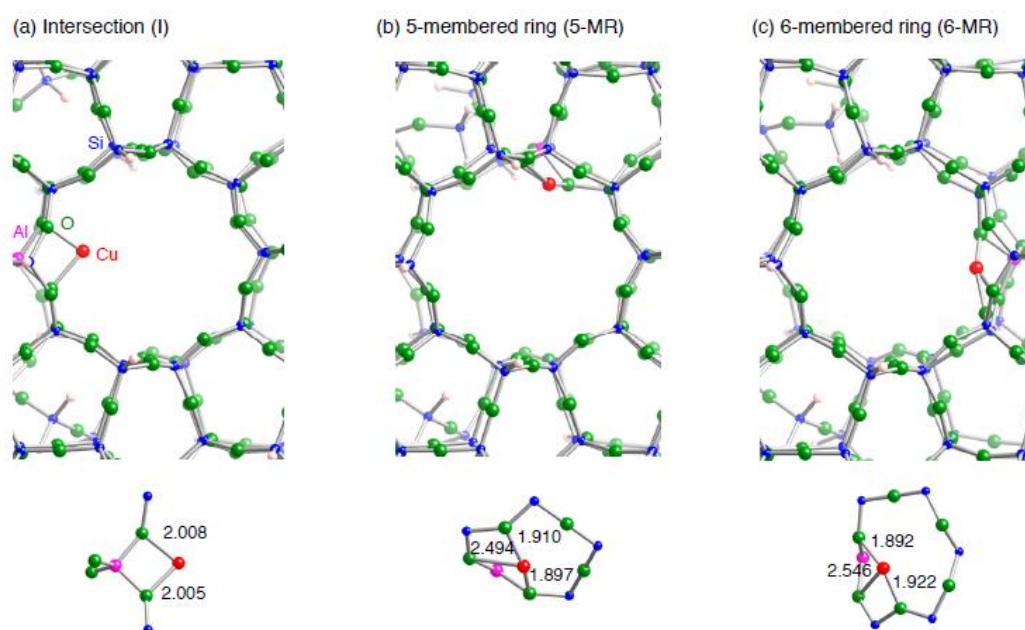
	Free $\text{C}_2\text{H}_4$			$\text{C}_2\text{H}_4$ on $\text{Cu}_1$ -zeolite	
	Symmetry	Frequency	IR intensity <sup>a</sup>	Frequency	IR intensity <sup>a</sup>
C≡C stretch	$A_g$	1645.2	0.00	1529.4	0.32
C–H stretch	$A_g$	3036.3	0.00	3023.9	0.00
C–H stretch	$B_{3g}$	3089.8	0.00	3090.7	0.00
C–H stretch	$B_{1u}$	3021.3	0.64	3017.7	0.98
C–H stretch	$B_{2u}$	3117.5	1	3113.2	1

<sup>a</sup> IR intensities are given relative to that of the C–H stretching mode spanning  $B_{2u}$ .

### 3.1.2. Realistic Cu<sub>1</sub>-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*– $\pi^*$  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 AlSi<sub>91</sub>O<sub>151</sub>H<sub>66</sub> 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.

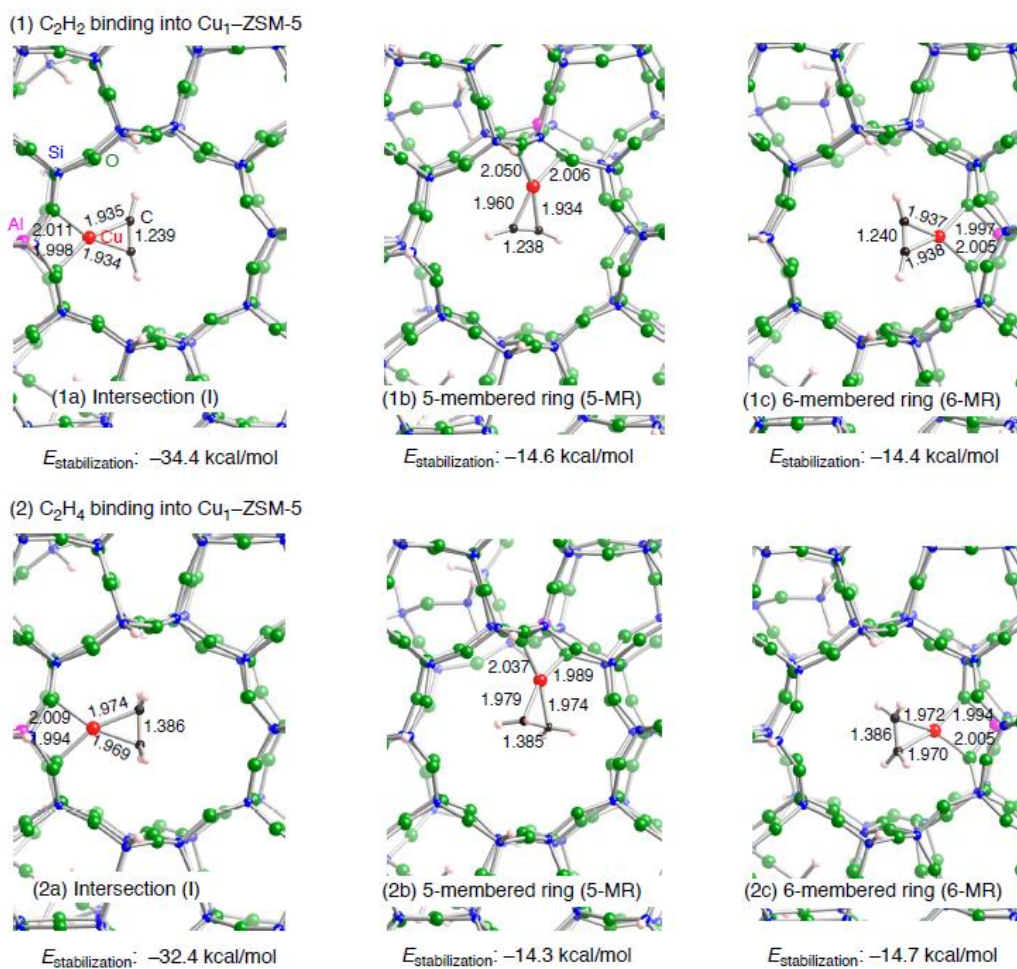
**Table 3.** Electronic configurations of Cu–ZSM-5 before and after the binding of an unsaturated hydrocarbon, based on natural atomic orbital analyses (NPA).

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

Optimized structures for unsaturated hydrocarbons adsorbed on a Cu<sub>1</sub>–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 ( $\eta^2$ -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  $\eta^2$ -fashion of the C<sub>2</sub>H<sub>2</sub> (C<sub>2</sub>H<sub>4</sub>) 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  $\eta^2$ -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 (C<sub>2</sub>H<sub>2</sub>) and −32.4 (C<sub>2</sub>H<sub>4</sub>) kcal/mol) are more pronounced than those in the **5-MR** configuration (−14.6 (C<sub>2</sub>H<sub>2</sub>) and −14.3 (C<sub>2</sub>H<sub>4</sub>) kcal/mol) and the **6-MR** configuration (−14.4 (C<sub>2</sub>H<sub>2</sub>) and −14.7 (C<sub>2</sub>H<sub>4</sub>) 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 <sup>a</sup>	Adsorbent	Binding mode	Cu-C <sup>b</sup>	CC <sup>b</sup>	$E_{\text{stabilization}}$ <sup>c</sup>	$E(\text{deform})$ <sup>d</sup>
<b>I</b>	C <sub>2</sub> H <sub>2</sub>	$\eta^2$	1.934, 1.935	1.239	−34.4	2.6
<b>5MR</b>	C <sub>2</sub> H <sub>2</sub>	$\eta^2$	1.934, 1.960	1.238	−14.6	20.4
<b>6MR</b>	C <sub>2</sub> H <sub>2</sub>	$\eta^2$	1.937, 1.938	1.240	−14.4	22.5
<b>I</b>	C <sub>2</sub> H <sub>4</sub>	$\eta^2$	1.969, 1.974	1.386	−32.4	2.3
<b>5MR</b>	C <sub>2</sub> H <sub>4</sub>	$\eta^2$	1.974, 1.979	1.385	−14.3	17.8
<b>6MR</b>	C <sub>2</sub> H <sub>4</sub>	$\eta^2$	1.970, 1.972	1.386	−14.7	20.3

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

In fact the  $E(\text{deform})$  values in the **I** configuration (2.6 (C<sub>2</sub>H<sub>2</sub>) and 2.3 (C<sub>2</sub>H<sub>4</sub>) kcal/mol) are negligible relative to those in the **5-MR** configuration (20.4 (C<sub>2</sub>H<sub>2</sub>) and 17.8 (C<sub>2</sub>H<sub>4</sub>) kcal/mol) and the **6-MR** configuration (22.5 (C<sub>2</sub>H<sub>2</sub>) and 20.3 (C<sub>2</sub>H<sub>4</sub>) 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  $\eta^2$ -bindings require larger displacement of copper cations rather than the  $\eta^1$ -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 ( $\text{Cu}_2$ -ZSM-5)

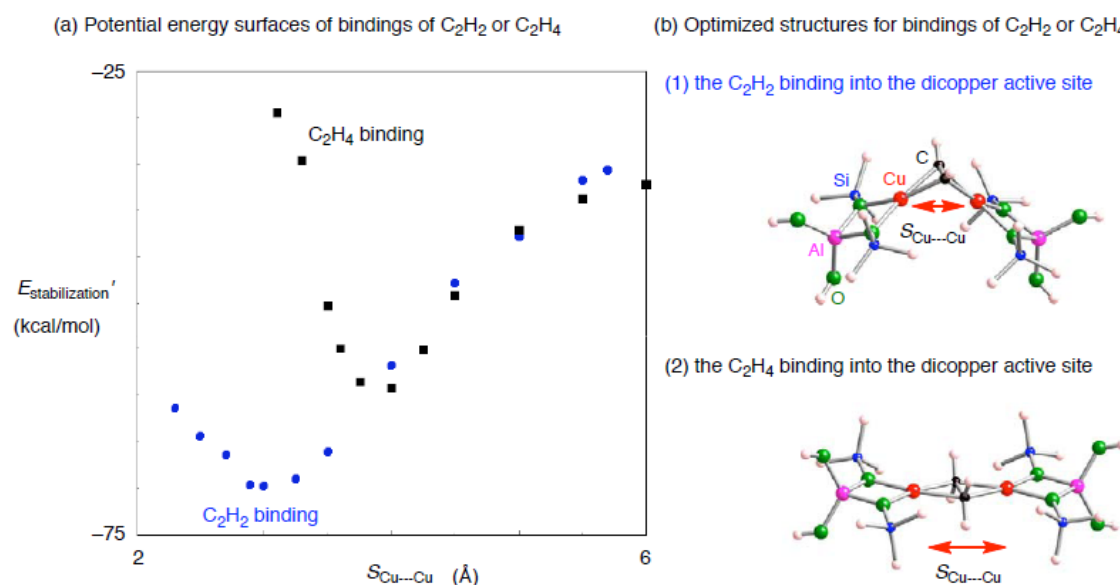
In this section we will focus on an unsaturated hydrocarbon bound to a dicopper active center embedded in ZSM-5. In this situation, configurations of the two copper cations within a ZSM-5 cavity may be responsible for the unsaturated hydrocarbon bindings, in addition to their copper coordination environment. 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  $\text{Cu}_2$ -zeolite taken from the optimized adsorbent- $\text{Cu}_2$ -zeolite[ $S_{\text{Cu}\cdots\text{Cu}}$ ] structure. When  $S_{\text{Cu}\cdots\text{Cu}}$  is 6 Å,  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_4$  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  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  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  $\text{Cu-C}$  bonds are newly generated. As a result, an unsaturated hydrocarbon binds into both copper cations in a  $\mu\text{-}\eta^2$ :  $\eta^2$  fashion. Because of the new  $\text{Cu-C}$  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  $\text{C}_2\text{H}_2$ -dicopper ( $\text{C}_2\text{H}_4$ -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  $\sim 6$  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 <sup>a</sup>	CC <sup>a</sup>	$S_{Cu\cdots Cu}$ <sup>b</sup>	$E_{\text{stabilization}}$ <sup>c</sup>
$C_2H_2$	$\mu-\eta^2:\eta^2$	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			

<sup>a</sup> Bond lengths in Å.; <sup>b</sup>  $S_{Cu\cdots Cu}$  is the  $Cu\cdots Cu$  separation in Å.; <sup>c</sup>  $E_{\text{stabilization}}$  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 Cu<sub>2</sub>C<sub>2</sub> 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<sup>-1</sup>) of CC and CH stretching modes of C<sub>2</sub>H<sub>2</sub> before and after the binding into the small dicopper zeolite model.

	Free C <sub>2</sub> H <sub>2</sub>			C <sub>2</sub> H <sub>2</sub> on Cu <sub>2</sub> -zeolite	
	Symmetry	Frequency	IR intensity <sup>a</sup>	Frequency	IR intensity <sup>a</sup>
C≡C stretch	Σ <sub>g</sub> <sup>+</sup>	2001.4	0.00	1557.1	1.44
C–H stretch	Σ <sub>g</sub> <sup>+</sup>	3400.0	0.00	3170.0	0.90
C–H stretch	Σ <sub>u</sub> <sup>+</sup>	3300.5	1	3127.8	1

<sup>a</sup> IR intensities are given relative to that of the C–H stretching mode spanning Σ<sub>u</sub><sup>+</sup>.

**Table 7.** Calculated vibrational frequencies (cm<sup>-1</sup>) of CC and CH stretching modes of C<sub>2</sub>H<sub>4</sub> before and after the binding into the small dicopper zeolite model.

	Free C <sub>2</sub> H <sub>4</sub>			C <sub>2</sub> H <sub>4</sub> on Cu <sub>2</sub> -zeolite	
	Symmetry	Frequency	IR intensity <sup>a</sup>	Frequency	IR intensity <sup>a</sup>
C≡C stretch	A <sub>g</sub>	1645.2	0.00	1469.4	0.00
C–H stretch	A <sub>g</sub>	3036.3	0.00	3004.9	0.00
C–H stretch	B <sub>3g</sub>	3089.8	0.00	3085.4	0.00
C–H stretch	B <sub>1u</sub>	3021.3	0.64	3001.8	17.10
C–H stretch	B <sub>2u</sub>	3117.5	1	3100.5	1

<sup>a</sup> IR intensities are given relative to that of the C–H stretching mode spanning B<sub>2u</sub>.

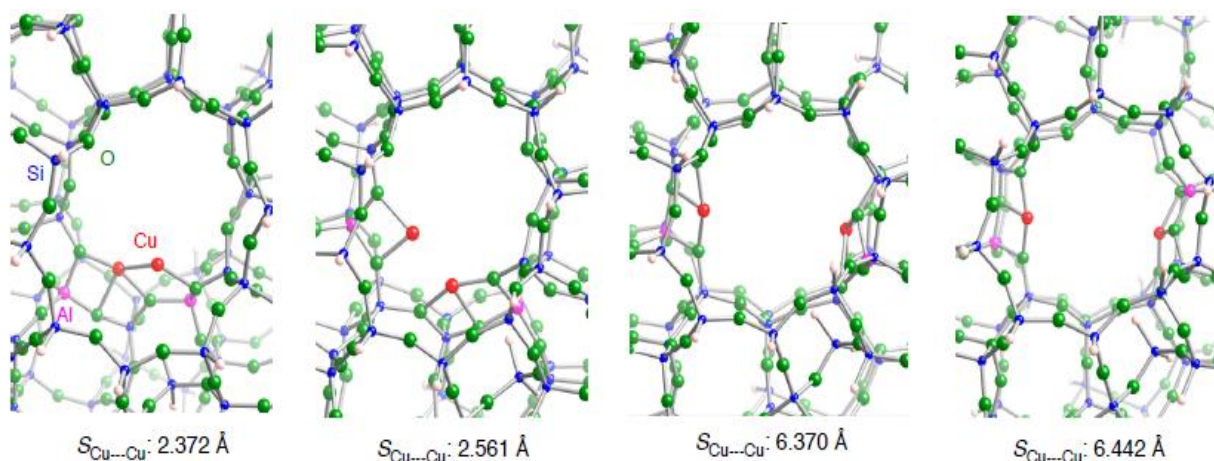
### 3.2.2. Realistic Cu<sub>2</sub>–ZSM-5 model

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 Al<sub>2</sub>Si<sub>90</sub>O<sub>151</sub>H<sub>60</sub>. 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 Cu<sub>2</sub>–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

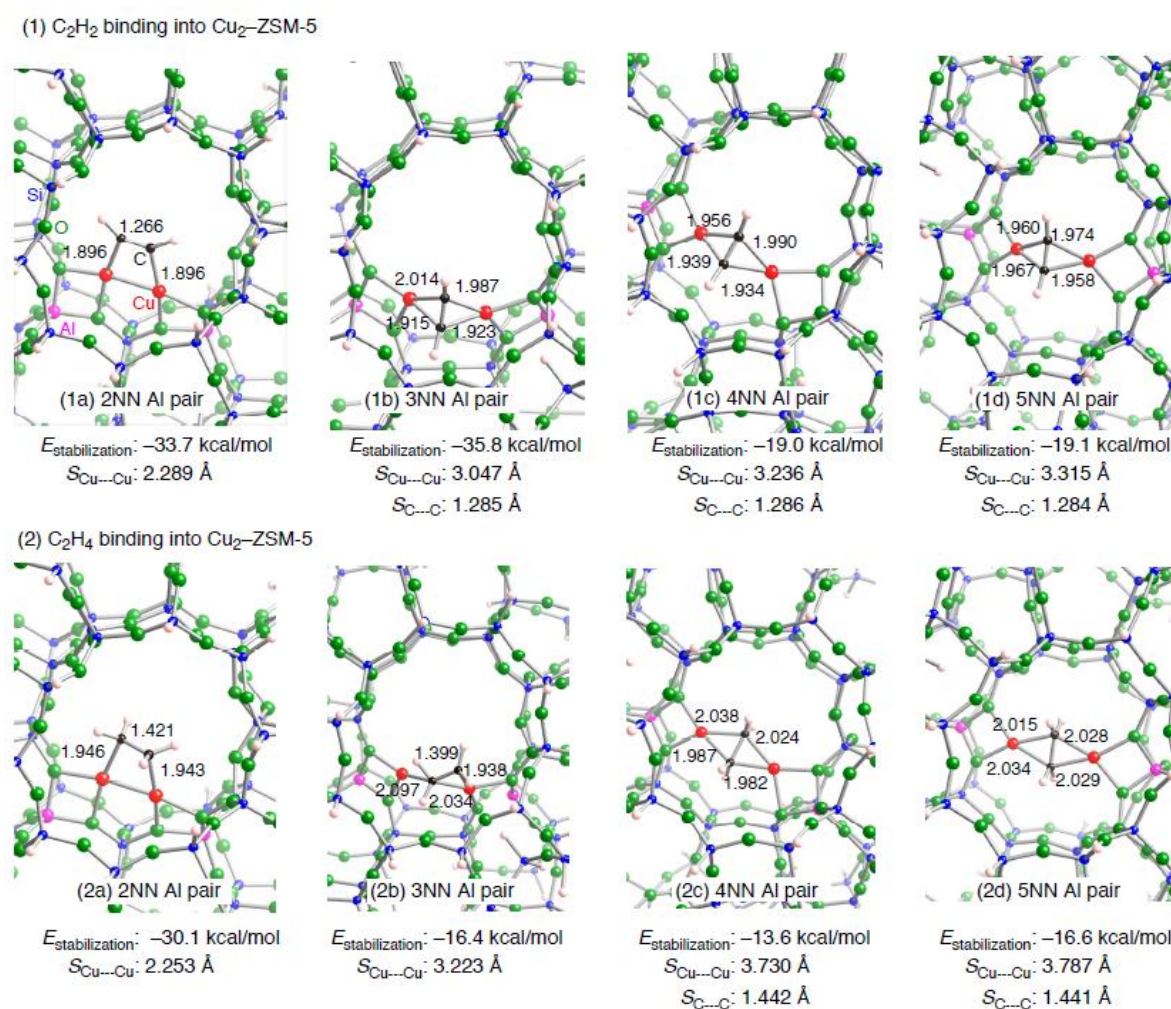
obtained by EXAFS analyses (2.47–3.13 Å). In the optimized Cu<sub>2</sub>–ZSM-5 structures, each Cu cation coordinates into two or three framework oxygen atoms. The Cu•••Cu separations are out of the range of a suitable span between the two copper cations into which an unsaturated hydrocarbon preferentially binds in a  $\mu$ - $\eta^2$ :  $\eta^2$ -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 C<sub>2</sub>H<sub>2</sub> into a dicopper active center. In the **2NN** configuration, C<sub>2</sub>H<sub>2</sub> binds into the dicopper active center in a  $\mu$ - $\eta^1$ :  $\eta^1$  fashion, whereas the **3NN**, **4NN**, and **5NN** configurations have a  $\mu$ - $\eta^2$ :  $\eta^2$  Cu<sub>2</sub>C<sub>2</sub> 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  $S_{\text{Cu}\cdots\text{Cu}}$  values are close to the separation between the two copper cations into which C<sub>2</sub>H<sub>2</sub> binds in a  $\mu$ - $\eta^2$ :  $\eta^2$  fashion in Figure 5. The significant differences in the  $S_{\text{Cu}\cdots\text{Cu}}$  values between before and after the C<sub>2</sub>H<sub>2</sub> 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 C<sub>2</sub>H<sub>2</sub> binding in a  $\mu$ - $\eta^2$ :  $\eta^2$  fashion. Instead, the **2NN** configuration adopts the  $\mu$ - $\eta^1$ :  $\eta^1$  binding fashion with a stabilization energy of −33.7 kcal/mol. Surprisingly the  $E_{\text{stabilization}}$  value is comparable to that of the **3NN** configuration (−35.8 kcal/mol), despite the different C<sub>2</sub>H<sub>2</sub> binding fashions.

**Figure 6.** Local structures of four optimized Cu<sub>2</sub>–ZSM-5 structures where the ZSM-5 framework was modeled as a Al<sub>2</sub>Si<sub>90</sub>O<sub>151</sub>H<sub>66</sub> 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...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  $\Delta S_{Cu...Cu}$  values. Table 8 shows that the  $\Delta S_{Cu...Cu}$  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 <sup>a</sup>	Adsorbent	Binding mode	Cu–C <sup>b</sup>	CC <sup>b</sup>	$S_{\text{Cu}\cdots\text{Cu}}$ <sup>c</sup> ( $\Delta S_{\text{Cu}\cdots\text{Cu}}$ <sup>d</sup> )	$E_{\text{stabilization}}$ <sup>e</sup>	$E(\text{deform})$ <sup>f</sup>
<b>2NN</b>	C <sub>2</sub> H <sub>2</sub>	$\mu-\eta^1: \eta^1$	1.896, 1.896	1.266	2.289 (–0.083)	–33.7	19.0
<b>3NN</b>	C <sub>2</sub> H <sub>2</sub>	$\mu-\eta^2: \eta^2$	1.915, 1.923, 1.987, 2.014	1.285	3.047 (0.486)	–35.8	24.7
<b>4NN</b>	C <sub>2</sub> H <sub>2</sub>	$\mu-\eta^2: \eta^2$	1.934, 1.939, 1.956, 1.990	1.286	3.236 (–3.134)	–19.0	45.7
<b>5NN</b>	C <sub>2</sub> H <sub>2</sub>	$\mu-\eta^2: \eta^2$	1.958, 1.960, 1.967, 1.974	1.284	3.315 (–3.127)	–19.1	47.2
<b>2NN</b>	C <sub>2</sub> H <sub>4</sub>	$\mu-\eta^1: \eta^1$	1.946, 1.943	1.421	2.253 (–0.119)	–30.1	18.0
<b>3NN</b>	C <sub>2</sub> H <sub>4</sub>	$\mu-\eta^1: \eta^2$	1.938, 2.034, 2.097	1.399	3.223 (0.662)	–16.4	25.5
<b>4NN</b>	C <sub>2</sub> H <sub>4</sub>	$\mu-\eta^2: \eta^2$	1.982, 1.987, 2.024, 2.038	1.442	3.730 (–2.640)	–13.6	41.9
<b>5NN</b>	C <sub>2</sub> H <sub>4</sub>	$\mu-\eta^2: \eta^2$	2.015, 2.028, 2.029, 2.034	1.441	3.787 (–2.655)	–16.6	43.1

<sup>a</sup> 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.; <sup>b</sup> Bond lengths in Å.; <sup>c</sup>  $S_{\text{Cu}\cdots\text{Cu}}$  is the Cu•••Cu separation in Å.; <sup>d</sup>  $\Delta S_{\text{Cu}\cdots\text{Cu}}$  is the difference in the Cu•••Cu separation between before and after the binding of an unsaturate hydrocarbon.; <sup>e</sup>  $E_{\text{stabilization}}$  in kcal/mol.; <sup>f</sup>  $E(\text{deform})$  in kcal/mol.

Compared with the C<sub>2</sub>H<sub>2</sub> bindings, more complicated binding modes are found in the C<sub>2</sub>H<sub>4</sub> 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 C<sub>2</sub>H<sub>4</sub> 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  $\text{C}_2\text{H}_4$  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  $\text{C}_2\text{H}_4$  binding is similar to that by the  $\text{C}_2\text{H}_2$  binding from a viewpoint of energetics. However, direct interactions by the  $\text{C}_2\text{H}_4$  binding are 11.0 kcal/mol weaker than those by the  $\text{C}_2\text{H}_2$  binding (see Table 5). Compared with the  $\text{C}_2\text{H}_2$  bindings, the importance of the destabilization by the cation shifts to determine a preferable  $\text{C}_2\text{H}_4$  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 ( $\eta^2$ ,  $\mu\text{-}\eta^1\text{:}\eta^1$ ,  $\mu\text{-}\eta^1\text{:}\eta^2$ , and  $\mu\text{-}\eta^2\text{:}\eta^2$  fashions) are expected in  $\text{Cu-ZSM-5}$ . The variety of characters of the copper-carbon bonds is unique in the restricted environment of a zeolite.

#### Acknowledgements

Support by Grants-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (No. 21655021).

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