

# **Adsorption of Copper Clusters in the TS-1 Pores:**

## **Ti versus Si and Gold versus Copper**

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### **Supporting Information:**

#### **1. Effect of Neglecting the Partial Charges in UFF:**

The electrostatic coupling between QM and MM regions has been neglected in calculating the  $\Delta E_{\text{ads}}$  values reported in the manuscript. How the charge equalization (qeq) is handled becomes important in QM/MM calculations. The problem with Gaussian is that it assigns qeq charges to the “real system” (defined above). For “model system”, however, it assigns the qeq charges from the “real system” directly, and the link atoms are assigned zero qeq charge. This creates charge imbalance. Following recursive and time intensive methodology is required to address this issue:

- (1) Start with the initial geometry and perform geometry optimization including the qeq charges.
- (2) Take the final geometry and optimize it again including the qeq charges. Note that the final geometry from step (1) is not truly converged because of the charge imbalance mentioned above. We find that final geometry is obtained after 5-6 geometry optimization steps (very small changes in the geometry).
- (3) Take the final geometry from step (2) and optimize it again including the qeq charges, etc. This procedure needs to be repeated till the changes in the

geometries and ONIOM energies are minimal (convergence is reached). Only at this point one has truly converged energies which account for the qeq charges.

In Reference 50, for representative cases, the activation energies obtained using this recursive procedure (with qeq charges) were compared with those obtained from calculations which ignore the electrostatic coupling between QM and MM region. Relatively constant (3-4 kcal/mol) shifts in the activation energies were observed. Therefore, we thought that the trends in  $\Delta E_{\text{ads}}$  across the series of Cu clusters would be independent of whether qeq charges are included or not, and hence we had ignored the electrostatic coupling between QM and MM region. In addition, our QM-level model (11 T) is large enough to account for most of the local electrostatic interactions between  $\text{Cu}_n$  and TS-1.

To support this, we performed explicit calculations using the aforementioned recursive procedure to examine the effect of qeq charges on  $\Delta E_{\text{ads}}$  in representative cases that were computationally feasible. In the table below, these results are compared with the  $\Delta E_{\text{ads}}$  values (reported in the manuscript) obtained by ignoring the partial charges.

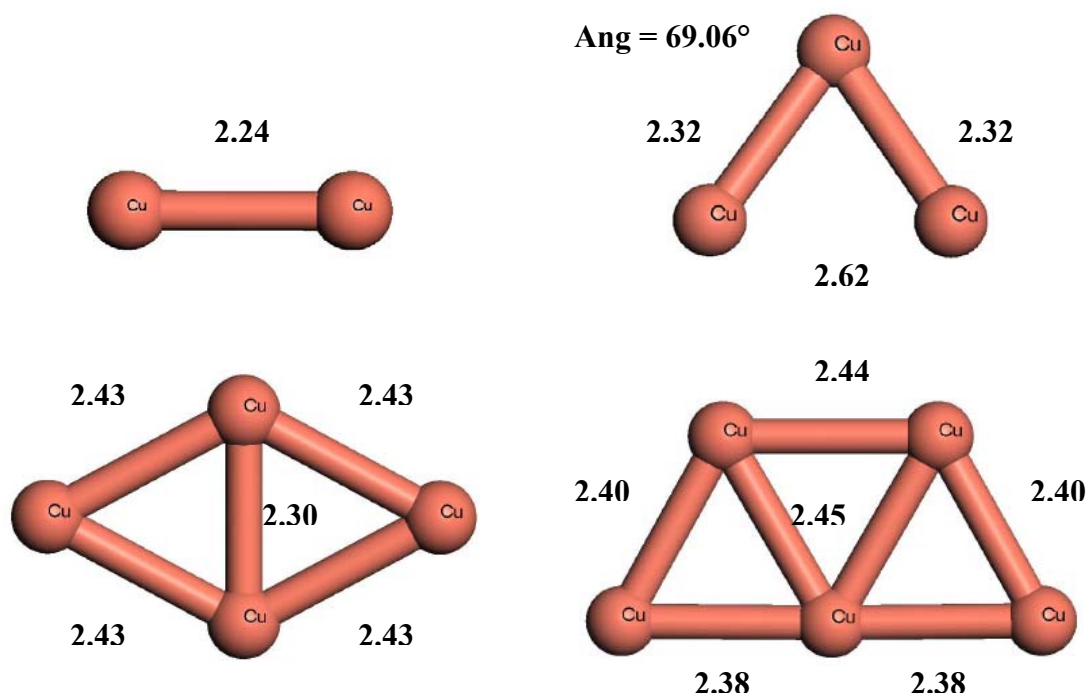
|                       | <b>Ti-non-defect Site</b>                                |   | <b>Si-non-defect Site</b>                                |   |
|-----------------------|--|---|--|---|
|                       | $\Delta E_{\text{ads}}$ (kcal/mol):<br>in the manuscript | $\Delta E_{\text{ads}}$ (kcal/mol):<br>with qeq charges | $\Delta E_{\text{ads}}$ (kcal/mol):<br>in the manuscript | $\Delta E_{\text{ads}}$ (kcal/mol):<br>with qeq charges |
| <b>Cu<sub>1</sub></b> | −11.76   | −15.51  | −6.82  | −8.27   |
| <b>Cu<sub>2</sub></b> | −17.25   | −20.28  | −14.03   | −15.56  |
| <b>Cu<sub>3</sub></b> | −31.62   | −33.19  | −19.12   | −20.09  |
| <b>Cu<sub>4</sub></b> | −27.19   | −30.34  | −20.38   | Not Completed   |
| <b>Cu<sub>5</sub></b> | −19.17   | Not Completed   | −10.32   | Not Completed   |

These representative results indicate that  $\Delta E_{\text{ads}}$  become more negative by 1-4 kcal/mol. Most importantly, the trends with respect to the cluster-size and Ti versus Si sites are unchanged. Therefore, the major results in our manuscript are independent of whether qeq charges are included or not. (The effect of qeq charges on  $\Delta E_{\text{ads}}$  appears to be opposite to that of BSSE corrections reported below. Luckily, this cancellation of errors reduces the uncertainty of the  $\Delta E_{\text{ads}}$  values reported in the manuscript.)

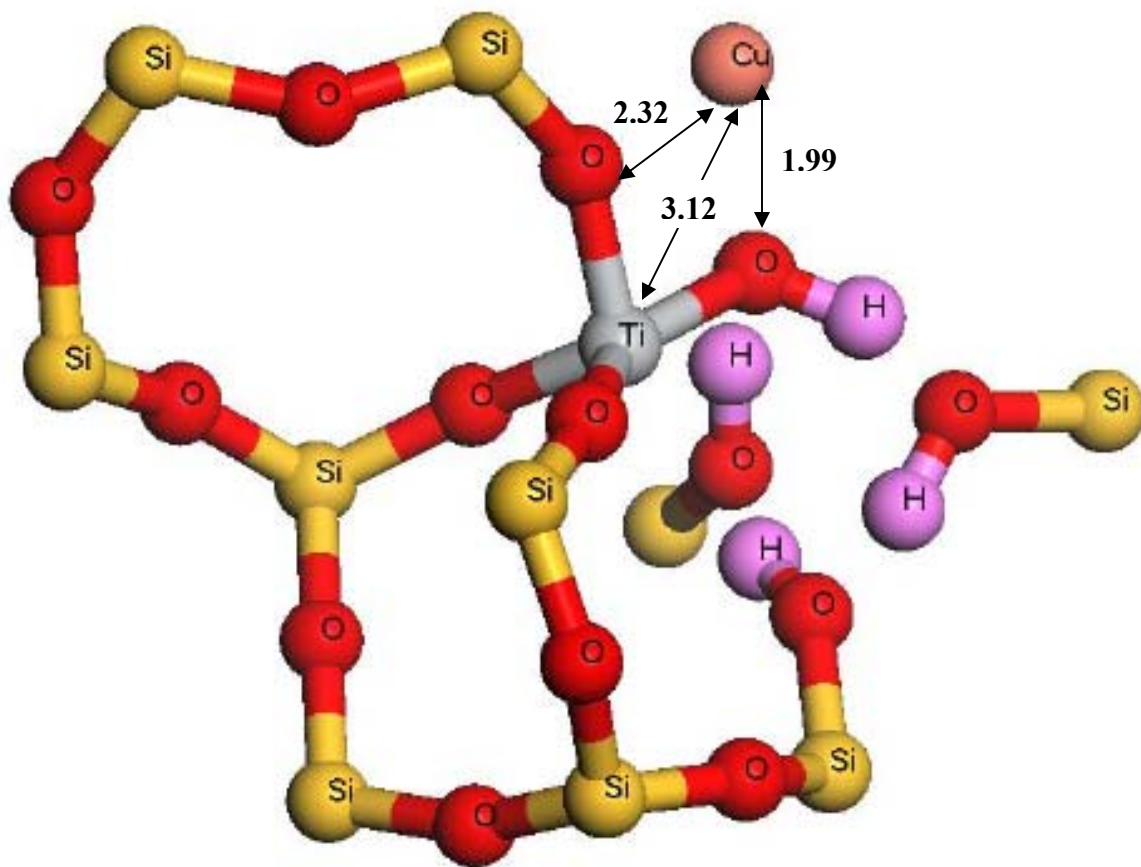
## 2. Analysis of Basis Set Superposition Errors (BSSE):

The BSSE in adsorption energies of Cu clusters in TS-1 pores were not calculated because the Gaussian03 software currently does not have the facility of performing counterpoise BSSE corrections in ONIOM (QM/MM) calculations. Therefore, we could not correct the adsorption energies reported in the paper. However, we can calculate BSSE corrections using pure QM calculations as follows. As stated in the manuscript, we have performed pure QM calculations on adsorption of Cu clusters on Ti-defect site. We utilized these pure QM calculations to estimate the BSSE corrections using the counterpoise method. We find that the BSSE corrections in the adsorption energies are up to 4 kcal/mol ( $\Delta E_{\text{ads}}$  becomes less negative). These values are tabulated below. Clearly, these corrections are only approximate because they were calculated using converged geometries in pure QM calculations and not in QM/MM calculations. Similar corrections are likely for Cu clusters adsorbed on non-defect sites.

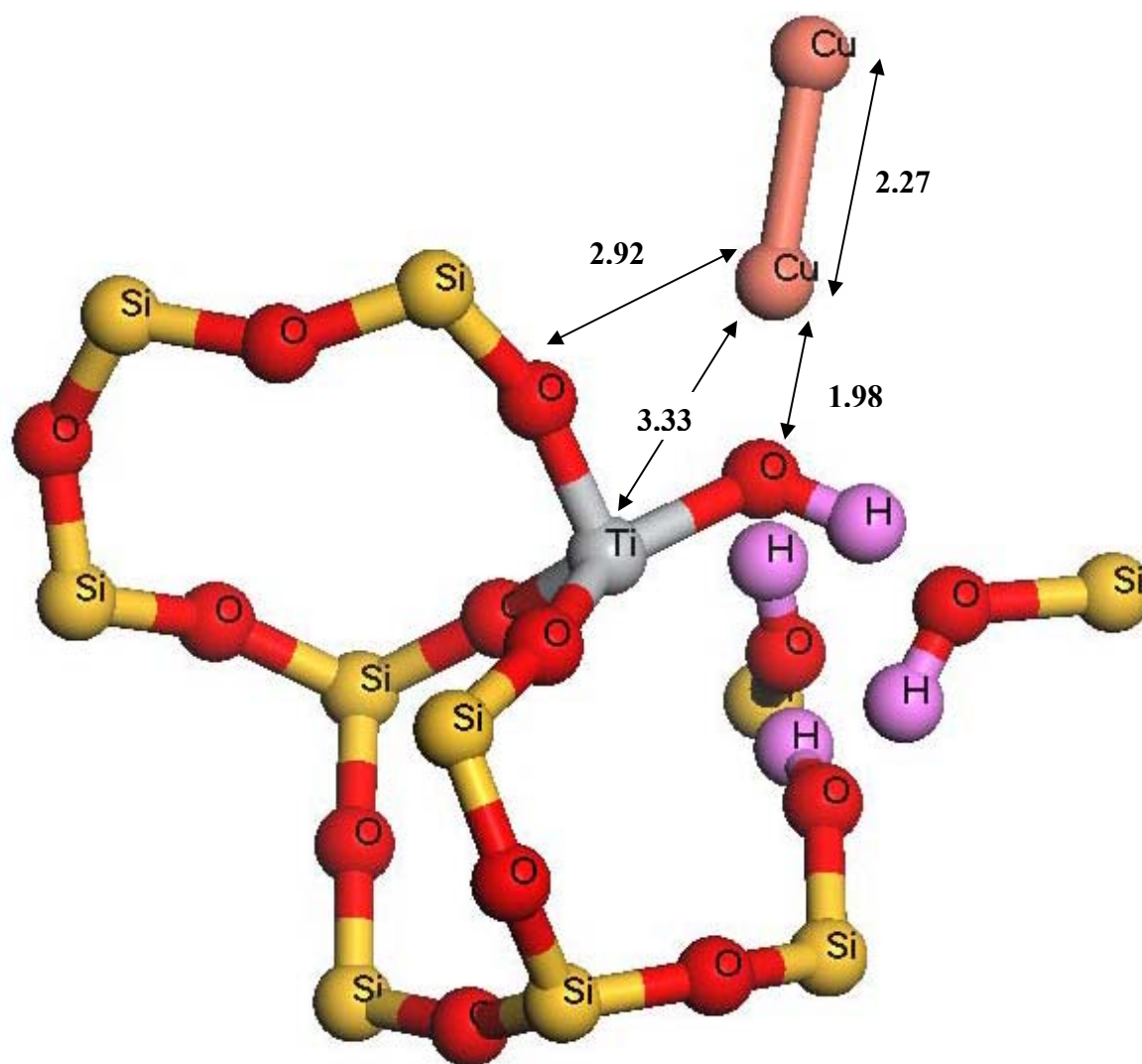
|                 | Cu <sub>1</sub> /Ti-def. | Cu <sub>2</sub> /Ti-def. | Cu <sub>3</sub> /Ti-def. | Cu <sub>4</sub> /Ti-def. | Cu <sub>5</sub> /Ti-def. |
|-----------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| BSSE (kcal/mol) | 3.10                     | 4.00                     | 3.70                     | 2.95                     | 2.98                     |



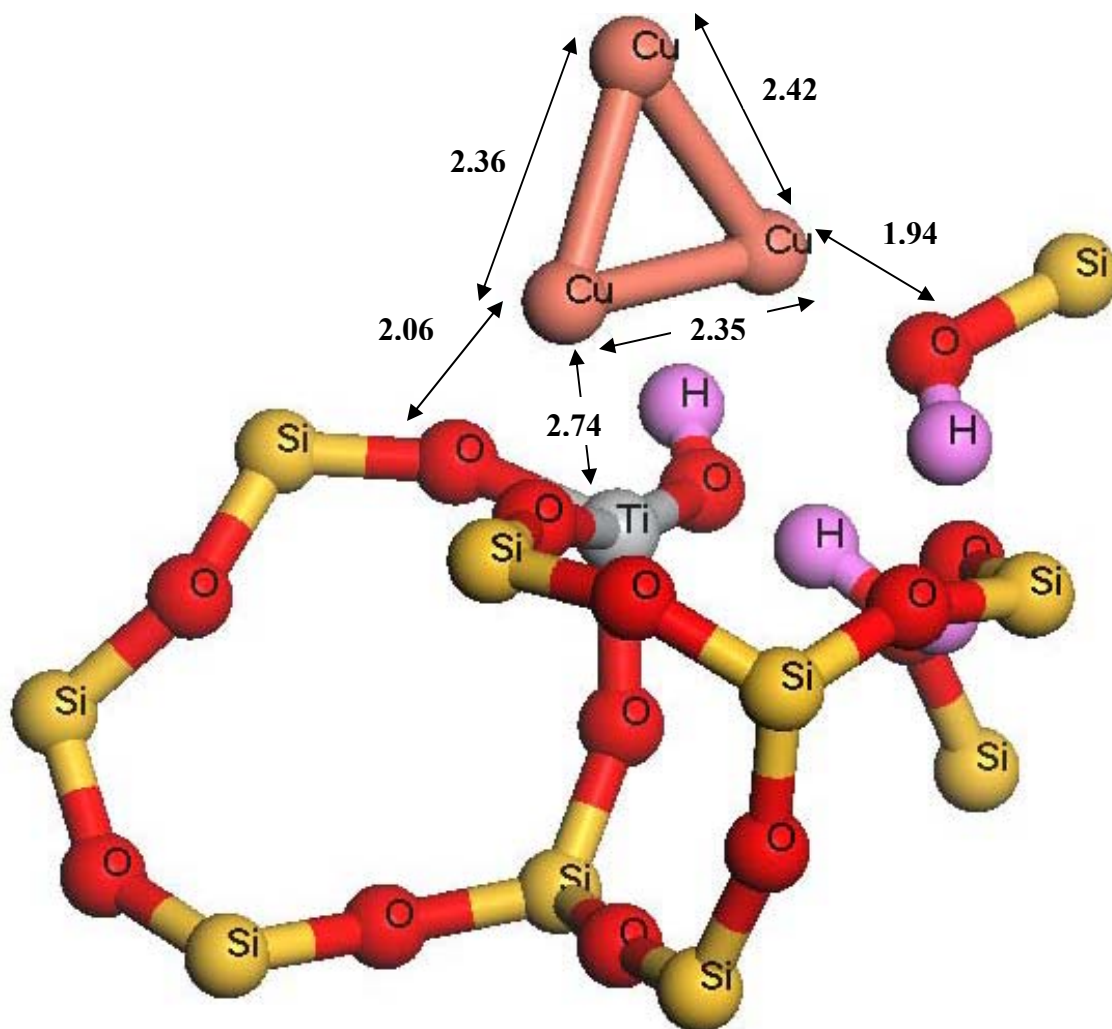
**Figure A.** The ground state geometries of unsupported (gas-phase)  $\text{Cu}_{2-5}$  clusters. All these geometries are planar and non-planar geometries are more than 8.5 kcal/mol higher in energy than the ground state geometries reported here. The Y-shaped  $\text{Cu}_4$  geometry is 8.2 kcal/mol higher in energy than the ground state (rhombus)  $\text{Cu}_4$  geometry reported here. The numbers represent the atomic distances in Å.



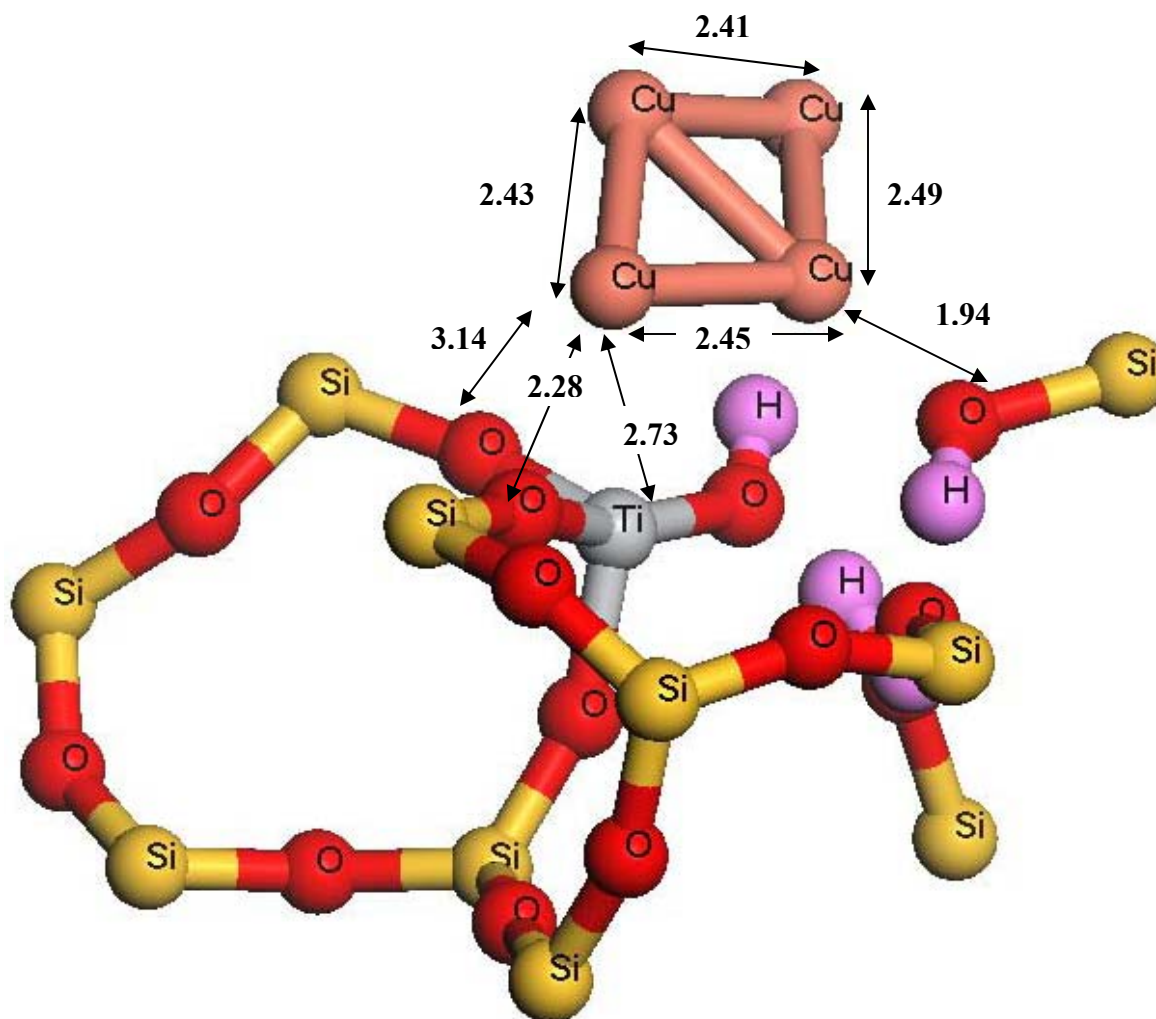
**Figure B.** Cu<sub>1</sub> adsorbed on the T6-Ti-defect site of the TS-1 lattice. All the MM atoms and some QM atoms are removed for clarity. The numbers near arrows represent the atomic distances in Å.



**Figure C.**  $\text{Cu}_2$  adsorbed on the  $\text{Ti}_6\text{-Ti}$ -defect site of the TS-1 lattice. All the MM atoms and some QM atoms are removed for clarity. The numbers near arrows represent the atomic distances in Å.

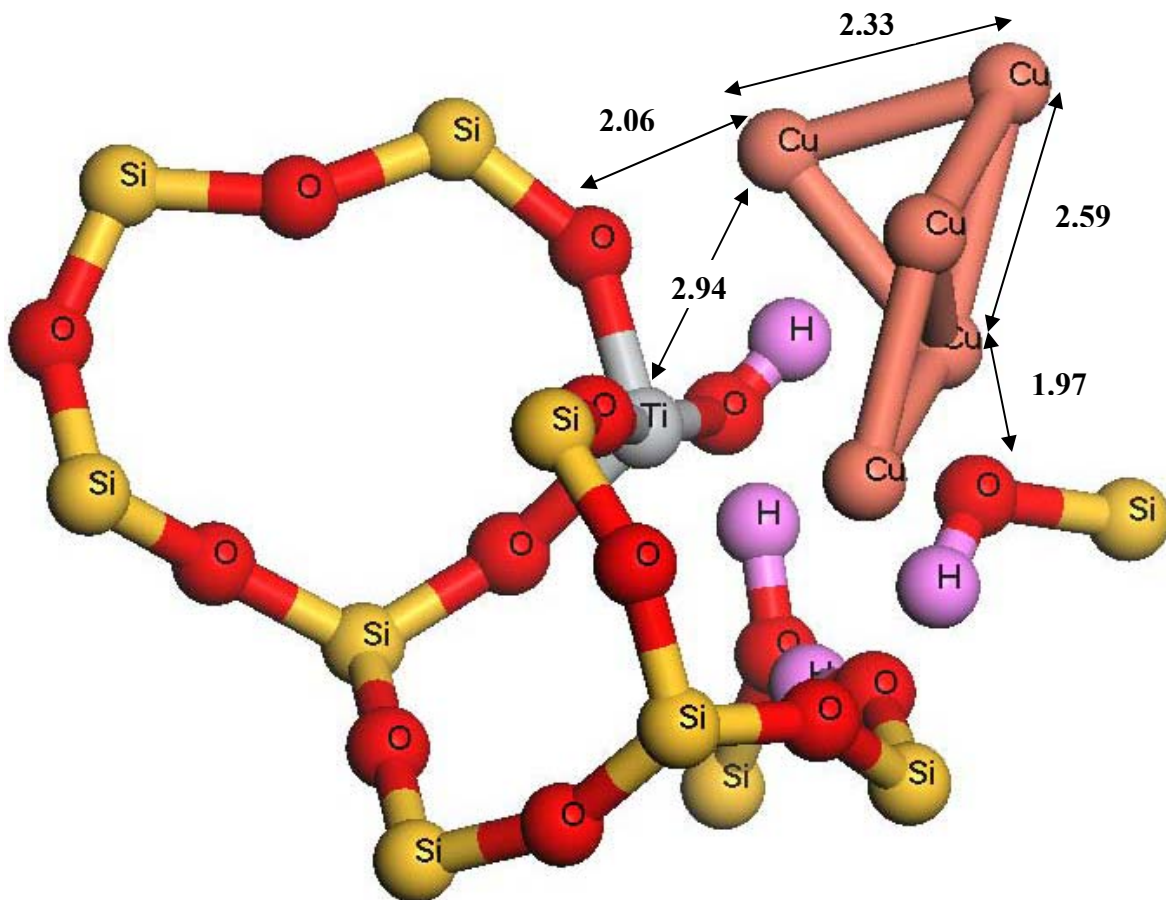


**Figure D.**  $\text{Cu}_3$  adsorbed on the T6-Ti-defect site of the TS-1 lattice. All the MM atoms and some QM atoms are removed for clarity. The numbers near arrows represent the atomic distances in Å.



**Figure E.**  $\text{Cu}_4$  adsorbed on the T6-Ti-defect site of the TS-1 lattice. All the MM atoms and some QM atoms are removed for clarity. The numbers near arrows represent the atomic distances in Å. The adsorbed  $\text{Cu}_4$  geometry is planar.





**Figure F.**  $\text{Cu}_5$  adsorbed on the T6-Ti-defect site of the TS-1 lattice. All the MM atoms and some QM atoms are removed for clarity. The numbers near arrows represent the atomic distances in Å. The adsorbed  $\text{Cu}_5$  geometry is non-planar.

### 3. Mulliken Charge-distribution on different atoms in Cu<sub>1-5</sub>/TS-1 geometries:

The charge-distribution of Cu<sub>1-5</sub> clusters adsorbed on different sites in TS-1 is shown in the table below. In the Cu<sub>2-5</sub> clusters, some atoms are positively charged and some atoms are negatively charged (charge-polarization). The positively charged Cu atoms are located close to the negatively charged lattice oxygens, while the negatively charged Cu atoms are located further away from the lattice oxygens. Therefore, the overall coulomb interactions are favorable.

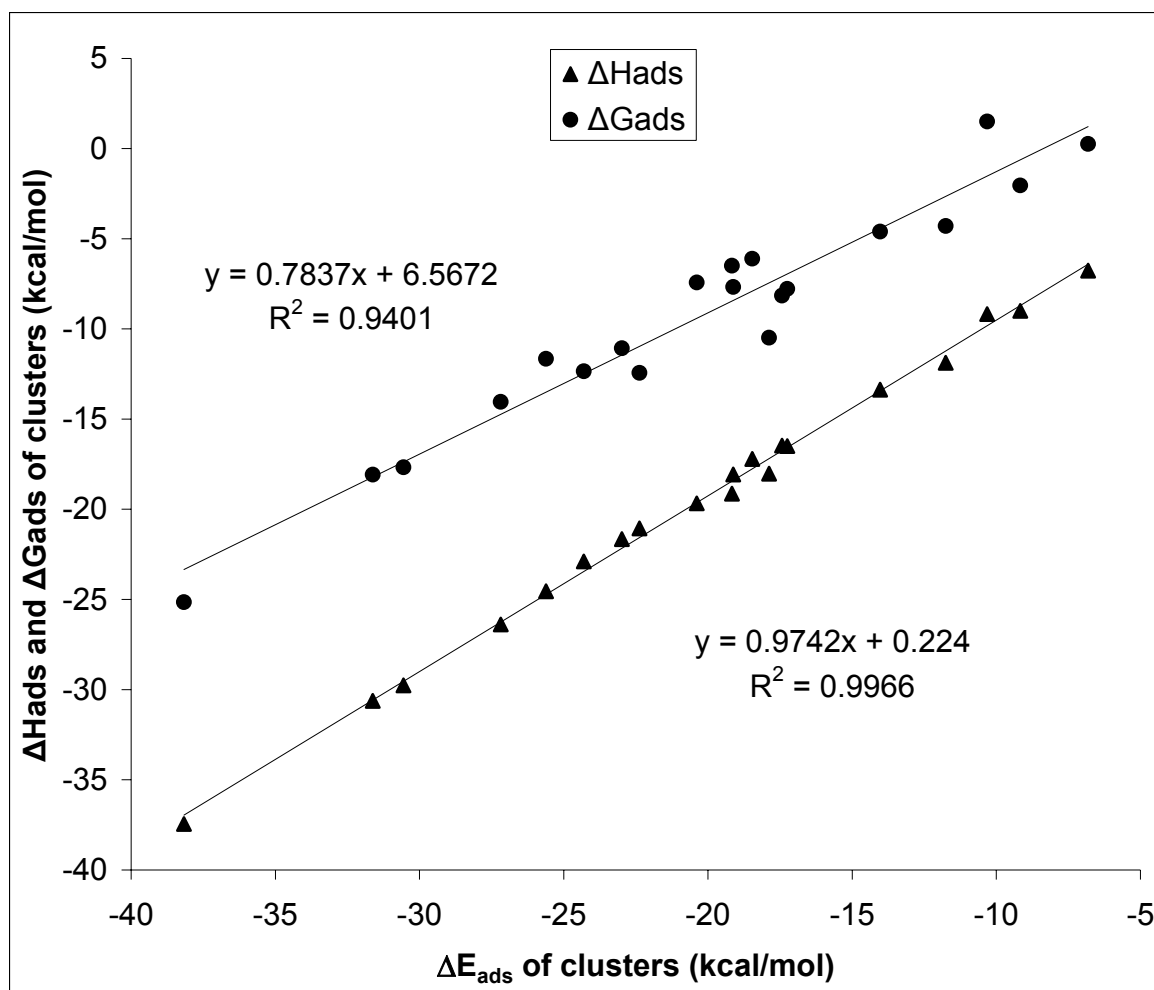
| Cluster               | Mulliken Charge on Cu Atoms of the Cu <sub>1-5</sub> Clusters Adsorbed on Different T6 Sites in TS-1 |               |               |               |
|-----------------------|--|---------------|---------------|---------------|
|                       | Ti-Non-Defect  | Si-Non-Defect | Ti-Defect     | Si-Defect     |
| <b>Cu<sub>1</sub></b> | <b>+0.130</b>  | <b>−0.052</b> | <b>+0.047</b> | <b>−0.106</b> |
| <b>Cu<sub>2</sub></b> | <b>−0.023</b>  | <b>−0.067</b> | <b>−0.163</b> | <b>−0.138</b> |
| Atom 1                | +0.035   | +0.043        | −0.070        | −0.021        |
| Atom 2                | −0.058   | −0.110        | −0.093        | −0.117        |
| <b>Cu<sub>3</sub></b> | <b>+0.345</b>  | <b>−0.075</b> | <b>+0.353</b> | <b>−0.168</b> |
| Atom 1                | +0.142   | −0.167        | −0.011        | +0.203        |
| Atom 2                | +0.178   | −0.118        | +0.211        | −0.190        |
| Atom 3                | +0.025   | +0.210        | +0.153        | −0.181        |
| <b>Cu<sub>4</sub></b> | <b>+0.027</b>  | <b>−0.101</b> | <b>−0.047</b> | <b>−0.171</b> |
| Atom 1                | +0.080   | −0.033        | +0.067        | +0.256        |
| Atom 2                | −0.026   | −0.040        | +0.173        | −0.179        |
| Atom 3                | −0.022   | +0.095        | −0.205        | −0.199        |
| Atom 4                | −0.005   | −0.123        | −0.082        | −0.049        |
| <b>Cu<sub>5</sub></b> | <b>+0.321</b>  | <b>−0.073</b> | <b>+0.105</b> | <b>−0.163</b> |
| Atom 1                | +0.107   | −0.040        | −0.066        | −0.017        |
| Atom 2                | −0.111   | −0.030        | −0.016        | −0.071        |
| Atom 3                | −0.072   | −0.260        | +0.137        | −0.267        |
| Atom 4                | +0.317   | +0.254        | +0.033        | +0.023        |
| Atom 5                | +0.080   | +0.003        | +0.017        | +0.169        |

**Table A. Thermochemical analysis of adsorption of Cu<sub>1-5</sub> clusters on nondefect sites inside the TS-1 pores at 298.15 K and 1 atm.  $\Delta U_{\text{ads}}$  is the internal energy of adsorption,  $\Delta H_{\text{ads}}$  is the enthalpy of adsorption,  $\Delta G_{\text{ads}}$  is the Gibbs free energy of adsorption, and  $T\Delta S_{\text{ads}}$  indicates the entropy change upon adsorption. The total Mulliken charge on the adsorbed clusters is also reported here. The “ $\Delta E_{\text{ads}}$ –better basis” column corresponds to the adsorption energies calculated at the BPW91/LANL2DZ/6-311+G(d, p):UFF level. All other data were calculated at the BPW91/LANL2DZ:UFF level. The nomenclature used to define the cluster binding mode ( $X_mO_n$ ) has been explained in the Section 3.4 of our paper.**

| Cluster<br>(Binding Mode)                          | $\Delta E_{\text{ads}}$<br>(kcal/mol) | $\Delta E_{\text{ads,ZPE}}$<br>(kcal/mol) | $\Delta U_{\text{ads}}$<br>(kcal/mol) | $\Delta H_{\text{ads}}$<br>(kcal/mol) | $\Delta G_{\text{ads}}$<br>(kcal/mol) | $T\Delta S_{\text{ads}}$<br>(kcal/mol) | $\Delta E_{\text{ads}}$ –better<br>basis<br>(kcal/mol) | Mulliken Charge<br>on Adsorbed Cu <sub>n</sub> |
|--|---------------------------------------|---|---------------------------------------|---------------------------------------|---------------------------------------|--|--|--|
| <b>Ti-non-defect site</b>                          |                                       |   |                                       |                                       |                                       |  |  |  |
| <b>Cu<sub>1</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –11.76                                | –11.87                                    | –11.29                                | –11.88                                | –4.29                                 | –7.58                                  | –10.43   | +0.130   |
| <b>Cu<sub>2</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –17.25                                | –17.00                                    | –15.90                                | –16.50                                | –7.78                                 | –8.72                                  | –16.33   | –0.023   |
| <b>Cu<sub>3</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | –31.62                                | –31.16                                    | –30.04                                | –30.63                                | –18.08                                | –12.55                                 | –27.11   | +0.345   |
| <b>Cu<sub>4</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | –27.19                                | –27.06                                    | –25.80                                | –26.39                                | –14.04                                | –12.35                                 | –23.75   | +0.027   |
| <b>Cu<sub>5</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | –19.17                                | –19.88                                    | –18.54                                | –19.13                                | –6.49                                 | –12.64                                 | –18.77   | +0.321   |
| <b>Si-non-defect site</b>                          |                                       |   |                                       |                                       |                                       |  |  |  |
| <b>Cu<sub>1</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –6.82                                 | –6.82                                     | –6.18                                 | –6.77                                 | +0.26                                 | –7.03                                  | –5.48  | –0.052   |
| <b>Cu<sub>2</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –14.03                                | –13.86                                    | –12.78                                | –13.37                                | –4.60                                 | –8.77                                  | –12.14   | –0.067   |
| <b>Cu<sub>3</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –19.12                                | –18.82                                    | –17.48                                | –18.07                                | –7.68                                 | –10.40                                 | –16.62   | –0.075   |
| <b>Cu<sub>4</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | –20.38                                | –20.39                                    | –19.08                                | –19.67                                | –7.43                                 | –12.24                                 | –16.58   | –0.101   |
| <b>Cu<sub>5</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | –10.32                                | –10.08                                    | –8.58                                 | –9.18                                 | +1.50                                 | –10.68                                 | –9.86  | –0.073   |

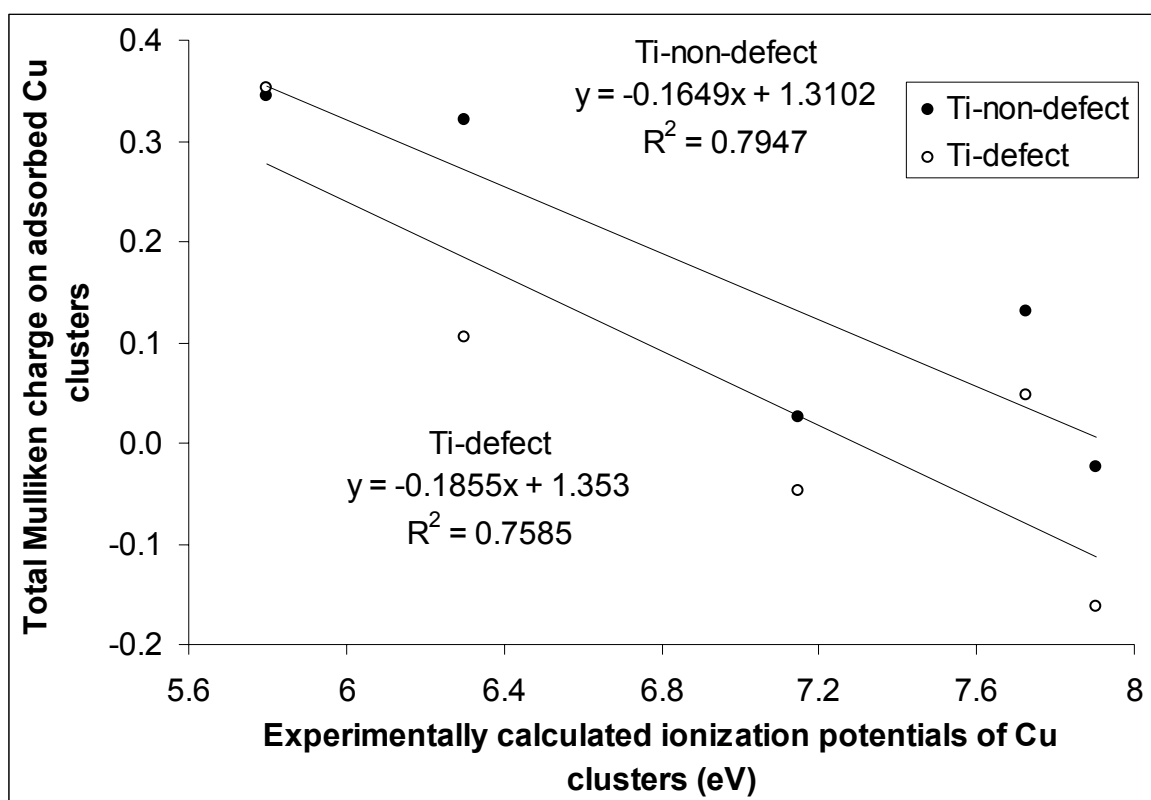
**Table B. Thermochemical analysis of adsorption of Cu<sub>1-5</sub> clusters on defect sites inside the TS-1 pores at 298.15 K and 1 atm.  $\Delta U_{\text{ads}}$  is the internal energy of adsorption,  $\Delta H_{\text{ads}}$  is the enthalpy of adsorption,  $\Delta G_{\text{ads}}$  is the Gibbs free energy of adsorption, and  $T\Delta S_{\text{ads}}$  indicates the entropy change upon adsorption. The total Mulliken charge on the adsorbed clusters is also reported here. The contribution of force fields to adsorption energies ( $\Delta E_{\text{ads,MM}}$ ) is included in the bracket for Cu<sub>1-5</sub> clusters adsorbed on Ti defect sites. The “ $\Delta E_{\text{ads}}-\text{better basis}$ ” column corresponds to the adsorption energies calculated at the BPW91/LANL2DZ/6-311+G(d, p):UFF level. All other data were calculated at the BPW91/LANL2DZ:UFF level.**

| Cluster<br>(Binding Mode)                          | $\Delta E_{\text{ads}}$ | $\Delta E_{\text{ads,ZPE}}$ | $\Delta U_{\text{ads}}$ | $\Delta H_{\text{ads}}$ | $\Delta G_{\text{ads}}$ | $T\Delta S_{\text{ads}}$ | $\Delta E_{\text{ads}}\text{--better}$<br>basis | Mulliken Charge on<br>Adsorbed Cu <sub>n</sub> |
|--|-------------------------|-----------------------------|-------------------------|-------------------------|-------------------------|--------------------------|---|--|
|  | (kcal/mol)              | (kcal/mol)                  | (kcal/mol)              | (kcal/mol)              | (kcal/mol)              | (kcal/mol)               | (kcal/mol)                                      |  |
| Ti-defect site                                     |                         |                             |                         |                         |                         |                          |   |  |
| <b>Cu<sub>1</sub> (X<sub>1</sub>O<sub>2</sub>)</b> | −17.88 (−5.67)          | −18.05                      | −17.44                  | −18.03                  | −10.48                  | −7.54                    | −16.75  | +0.047   |
| <b>Cu<sub>2</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | −22.37 (−7.25)          | −21.56                      | −20.47                  | −21.06                  | −12.43                  | −8.63                    | −20.67  | −0.163   |
| <b>Cu<sub>3</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | −38.17 (−8.37)          | −38.36                      | −36.86                  | −37.45                  | −25.15                  | −12.30                   | −37.05  | +0.353   |
| <b>Cu<sub>4</sub> (X<sub>2</sub>O<sub>2</sub>)</b> | −30.55 (−7.60)          | −30.68                      | −29.17                  | −29.76                  | −17.67                  | −12.09                   | −29.95  | −0.047   |
| <b>Cu<sub>5</sub> (X<sub>3</sub>O<sub>3</sub>)</b> | −25.61 (−7.20)          | −25.66                      | −23.96                  | −24.55                  | −11.65                  | −12.90                   | −24.56  | +0.105   |
| Si-defect site                                     |                         |                             |                         |                         |                         |                          |   |  |
| <b>Cu<sub>1</sub> (X<sub>1</sub>O<sub>1</sub>)</b> | −9.17                   | −9.13                       | −8.40                   | −9.00                   | −2.04                   | −6.96                    | −8.09   | −0.106   |
| <b>Cu<sub>2</sub> (X<sub>1</sub>O<sub>2</sub>)</b> | −17.43                  | −17.08                      | −15.88                  | −16.47                  | −8.15                   | −8.32                    | −17.11  | −0.138   |
| <b>Cu<sub>3</sub> (X<sub>1</sub>O<sub>2</sub>)</b> | −24.30                  | −23.69                      | −22.30                  | −22.89                  | −12.35                  | −10.54                   | −23.50  | −0.168   |
| <b>Cu<sub>4</sub> (X<sub>1</sub>O<sub>2</sub>)</b> | −22.98                  | −22.56                      | −21.06                  | −21.65                  | −11.07                  | −10.59                   | −22.33  | −0.171   |
| <b>Cu<sub>5</sub> (X<sub>1</sub>O<sub>2</sub>)</b> | −18.46                  | −18.10                      | −16.62                  | −17.21                  | −6.10                   | −11.11                   | −15.05  | −0.163   |

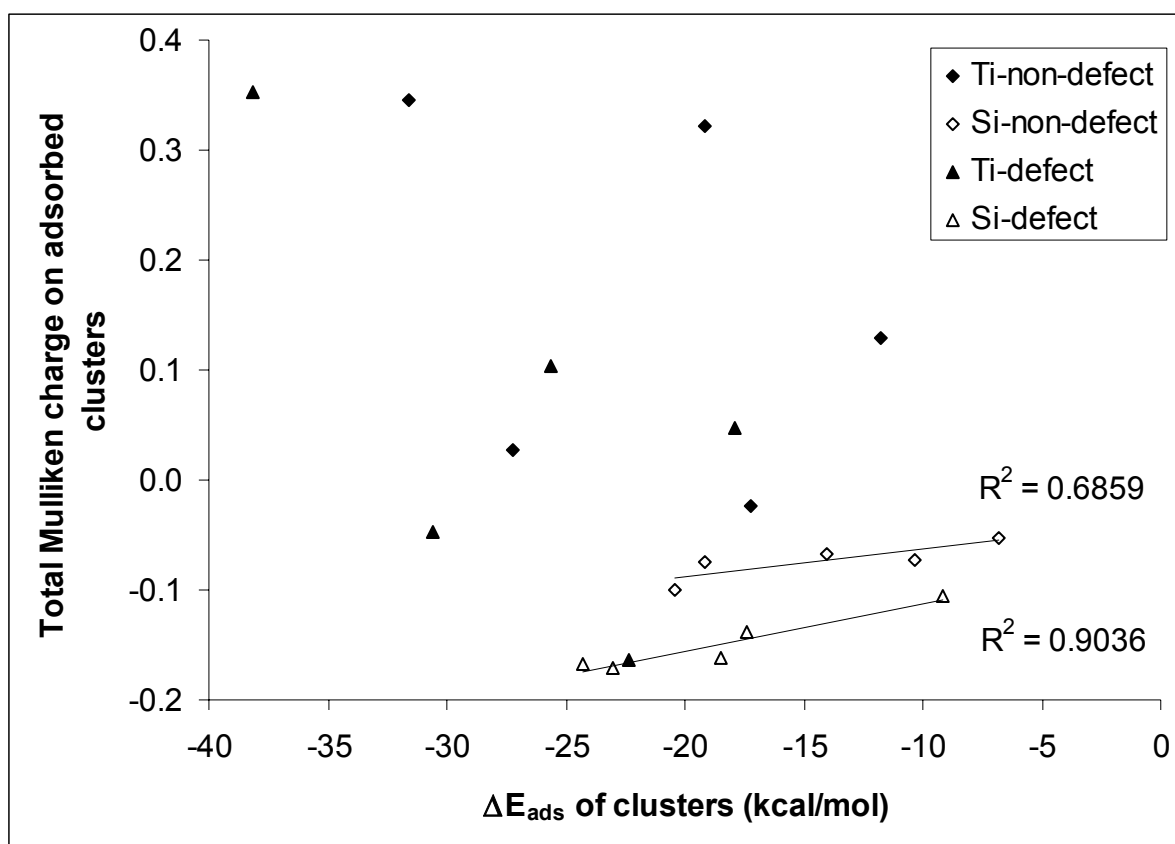


**Figure G. Linear relation between the  $\Delta E_{ads}$  of Cu clusters and other thermochemical quantities ( $\Delta H_{ads}$  and  $\Delta G_{ads}$ ). Similar relation is applicable also for  $\Delta E_{ads,ZPE}$  and  $\Delta U_{ads}$  (not shown).**

4. A plot of Mulliken charge on Cu clusters adsorbed on Ti sites versus experimentally calculated IP values shows approximate linear correlations (see below); the lower the IP, the higher is the electron-density transfer from the cluster to the TS-1 support, and the stronger is the cationic character of the adsorbed cluster.



5. In our previous work on Au clusters we found that the extent of charge-transfer from the TS-1 support to the adsorbed clusters is linearly correlated to the adsorption energy. However, for Cu clusters, we did not find any such correlation (see below). This is one of the key differences in the cluster-support interactions in Au/TS-1 and Cu/TS-1 systems.



6. The charge-transfer interactions between the  $\text{Cu}_{1-5}$  clusters adsorbed on the Ti sites in TS-1 versus the interactions between  $\text{Cu}_{1-5}$  clusters adsorbed on Si sites are quite different (see below). The trends in the Mulliken charges on Cu clusters adsorbed on Ti sites versus Si sites are completely different.

