

## Coordination and Siting of Cu<sup>+</sup> Ion Adsorbed into Silicalite-2 Porous Structure: A Density Functional Theory Study

M. Ghambarian<sup>a</sup>, M. Ghashghaee<sup>b</sup> and Z. Azizi<sup>c,\*</sup>

<sup>a</sup>Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box: 14975-112, Tehran, Iran

<sup>b</sup>Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box: 14975-112, Tehran, Iran

<sup>c</sup>Department of Chemistry, Karaj Branch, Islamic Azad University, P.O. Box: 31485-313, Karaj, Iran

(Received 23 July 2016, Accepted 24 October 2016)

Coordination of Cu<sup>+</sup> ions adsorbed on the plausible sites of a silicalite-2 lattice has been investigated computationally *via* hybrid density functional theory method at the B3LYP/6-311+G\* and B3LYP/Def2-TZVP levels using molecular models of the active site. The symmetrical coordination of Cu<sup>+</sup> ions to almost five oxygen atoms of the all-silica framework in six-membered ring (6MR) sites of the main channels was the most stable configuration of Cu-silicalite-2 clusters. On the contrary, the metal cation was found to be most weakly bound to the sites at the intersections where the metal ion was twofold coordinated. Implications on the catalytic chemistry for adsorption or activation of different molecules on the exchanged sites are discussed. The average binding energy was calculated to be ~46 kcal mol<sup>-1</sup> for Cu/silicalite-2. Although chemisorbed, the relatively weak bindings of Cu<sup>+</sup> supported some unusual reactivity of high-silica Cu-doped ZSM-11 catalysts in previous studies and evinced that this adsorbent can offer substantial capacities with respect to the guest molecules; *e.g.*, in pollution abatement.

**Keywords:** Copper, Silicalite-2, DFT, Adsorption, Nanoporous materials

### INTRODUCTION

Silicates and zeolites containing transition-metal ions (TMIs) offer high activity as heterogeneous catalysts for a wide range of reactions such as pollutants abatement and selective oxidation reactions [1-3]. Knowledge of the location (and accessibility), coordination and electronic structure of the TMI centers in the zeolite/silicate framework is of crucial importance for a fundamental understanding of the adsorptive/catalytic potential of these materials [2] and also to enable more systematic exploration of new sorbents or catalysts [4]. It is difficult, however, to investigate the metal-support interactions by means of surface science techniques because their nonconductive and brittle nature brings about difficulties in sample charging and heating. Theoretical studies, in particular, if

implemented with first-principle approaches, may be considered as useful complements to understand the microscopic phenomena [5].

ZSM-5, ZSM-11 and their pure silica forms (silicalite-1 and silicalite-2) are two of the most widely used materials in the zeolite family which triggered an immense research attempt in research institutes and academia to synthesize similar materials which eventually differed from the original zeolites in their chemical composition, their sorption capacity, or their catalytic activity, but not necessarily belonging to different structure types [6]. The lattice structures of both silicalite-1 and silicalite-2 are based on pentasil building units joined to form chains or columns, which are common to these frameworks [6-7]. Layers of such columns (so-called pentasil layers) may be linked across inversion centers as *i*-stacking or across mirror planes as  $\sigma$ -stacking to form the framework of ZSM-5 or ZSM-11, respectively [6-8]. The most symmetrical pentasil

\*Corresponding author. E-mail: [zahra.azizi@kiaui.ac.ir](mailto:zahra.azizi@kiaui.ac.ir)

observed is ZSM-11 with a tetragonal symmetry [6]. A low temperature high efficiency approach has been suggested for preparation of high quality ZSM-11 zeolites at 90 °C in 7–14 days employing non-pressurized equipment [9]. Hierarchical ZSM-11 or silicalite-2 crystals with intracrystalline mesoporosity have been synthesized and used in model isomerization, epoxidation, and cracking reactions [10-14]. For example, synthesized mesoporous H-ZSM-11 catalysts have shown extraordinary high activities in cracking of *n*-hexadecane, even higher than conventional microporous catalysts [10].

There exist a number of reports on experimental identification as well as theoretical modeling of copper ions in porous materials [15-20,21-41,42-50]. Copper catalysts have also been investigated for a wide range of reactions and adsorption processes [22,51,23,52,20,53,24, 54,13,55,46,56-58,1,59-63,38]. For instance, the ability of Cu<sup>+</sup> ions in zeolite framework to form an interesting  $\sigma$ -type adsorption complex with H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> has been stressed [38]. Also, the adsorption of small probe molecules such as NO, CO, NO<sub>2</sub>, N<sub>2</sub>O, SO<sub>x</sub>, N<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> on Cu<sup>+</sup> ions in zeolites of an MFI structure has been addressed in several studies [52,45,53,57,64,58,60,27,56,24,17,16,48,1,63,65,47, 28,19-20,42]. Copper-exchanged Y zeolite has further been investigated computationally for adsorption of various molecules [59]. As another example, quantum chemical calculations have demonstrated, in full agreement with IR measurements, that the NO molecule adsorbed on the Cu<sup>+</sup> site is more freely activated than on the Cu<sup>2+</sup> centre as evidenced by remarkably higher HOMO energies of the former [17]. In addition, the Cu<sup>I</sup>-exchanged zeolites are very promising sorbents for separation of olefins and desulfurization of fossil fuels [4].

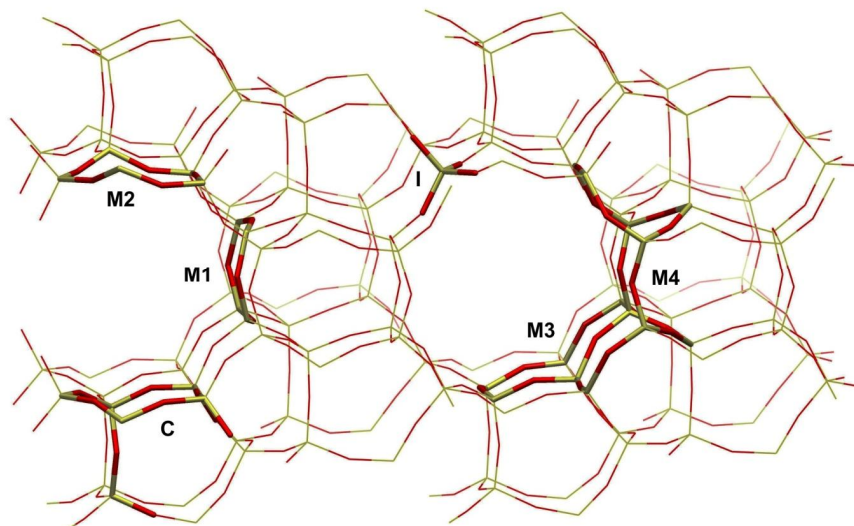
It has been inferred experimentally that high-silica zeolites can attain higher activities for NO decomposition [52,18]. An acceptable conversion rate was obtained, *e.g.*, for the reaction with Si/Al ratios higher than 30.9 with an ideal copper exchange of 150%, thus requiring partial reduction of the loaded metal ions [52]. Experimental studies have also demonstrated that both Cu/ZSM-11 (with MEL structure type with two-dimensional 10MR pores) and Cu/ZSM-12 (MTW structure of one-dimensional 12MR pores) are about twice as active as the most investigated zeolite Cu/ZSM-5 (MFI structure with straight and zig-

zag/sinusoidal channels) in direct decomposition of NO [30,13]. Nevertheless, relatively scant attention has been paid in computational studies to all-silica frameworks, in general, and zeolite structures such as ZSM-11 (silicalite-2), in particular, as an adsorbent or a catalyst support in the realm of TMI applications. The present work is then aimed to provide a preliminary study of a silicalite-2 framework to investigate the binding power, the local structure and the electronic properties of Cu<sup>+</sup> ions at these sites in the framework of density functional theory (DFT). It is also discussed that how different environments of Cu<sup>+</sup> ion can affect the adsorption interactions of a guest molecule.

## COMPUTATIONAL METHOD

Cluster modeling approach was used for the simulations. As a commonly adopted technique to embed clusters of covalent materials [40,22], all terminal broken bonds of the cluster were saturated by H atoms placed along the bond with the next oxygen or silicon atom excluded from the cluster in directions obtained from a perfect crystal. The crystallographic data for all-silica ZSM-11 structure was obtained from the literature [66].

Figure 1 defines the main individual Cu<sup>+</sup> sites in the ZSM-11 structure. The important plausible adsorption positions recognized here include intersection site I, ring sites of M1, M2, M3 and M4 representing the so-called 4MR, 5MR, 6MR and 8MR structures in the main channel, and another cage-like position designated as C. As shown in Fig. 2, the latter model may be viewed as a curved six-ring site located inside the walls of silicalite-2 which is composed of several fused five-rings. The coordination of Cu<sup>+</sup> to the above-mentioned sites of Cu-silicalite-2 was, respectively, represented by the Si<sub>5</sub>O<sub>4</sub>H<sub>12</sub>Cu, Si<sub>8</sub>O<sub>12</sub>H<sub>12</sub>Cu, Si<sub>5</sub>O<sub>15</sub>H<sub>9</sub>Cu, Si<sub>6</sub>O<sub>18</sub>H<sub>12</sub>Cu, Si<sub>10</sub>O<sub>16</sub>H<sub>16</sub>Cu and Si<sub>7</sub>O<sub>18</sub>H<sub>10</sub>Cu clusters with the overall charge set to +1 for the calculations. The cluster models are shown in Figs. 1 and 2. Hence, the sizes of the inner part ranged from T5 to T10 units. These cluster models are large enough to account for all of the interactions of the Cu<sup>+</sup> ion with the oxide framework. This kind of cluster modeling enables high-level calculations that result in precise local pictures of the adsorption sites in terms of geometry and spectroscopic features [40,67-68]. As proven to be effective in the



**Fig. 1.** Designation of important individual sites of Cu<sup>+</sup> and their positions in the silicalite-2 structure viewed at the (010) layer. The 10-membered rings represent the main channels of the framework where the ring-type M1, M2, M3 and M4 sites are located on the cavity walls. The I and C centers are located at the intersection of the straight channels and the cage-like space in the walls, respectively.

previous studies [5], the adsorbent cluster was kept fixed during the geometrical optimizations to provide a simple representation of the mechanical embedding of the solid matrix.

The present study made use of the Gaussian 98 quantum mechanical software package [69] for all of the calculations. The geometry optimizations of all structures were performed by using hybrid functional B3LYP method [70-72]. This approach has been widely used for studying of adsorption processes yielding reliable data both on oxides and metal clusters [21-22,73]. The standard 6-31+G\* Pople's basis set was applied on all of the atoms [74-77]. The improved energetic results were obtained by single-point calculations at the higher level of theory of B3LYP/6-311+G\* based on B3LYP/6-31+G\* geometries [78]. Another set of calculations were also carried out with the larger Def2-TZVP basis set [79-80] for comparison. The electronic charges were computed according to the natural bond orbital (NBO) method. The NBO population [81] analyses and those of the quantum theory of atoms in molecules (QTAIM) [82-87] on the optimized structures

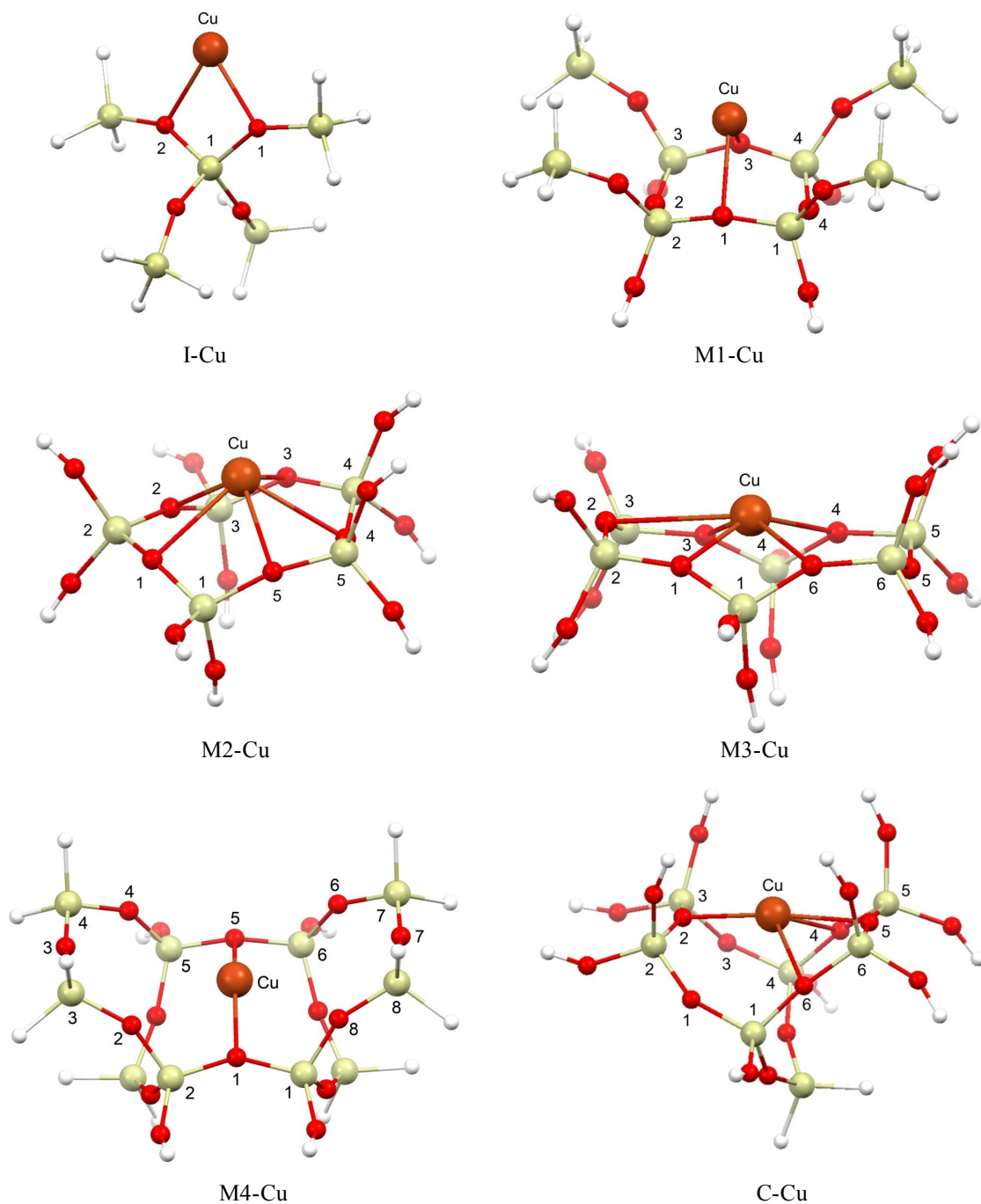
were accomplished at the B3LYP/6-311+G\* level of theory. The graphical output of the calculations was obtained by the molecular visualization program Mercury [88-91]. For all cluster models, a similar calculation was implemented on the bare clusters in the absence of metal ion to allow for an estimation of the adhesion or binding energy (*BE*) of Cu<sup>+</sup> at every site [25]:

$$BE = E_{\text{CuS}_2} - E_{\text{Cu}} - E_{\text{S}_2}$$

where  $E_{\text{Cu}}$ ,  $E_{\text{S}_2}$  and  $E_{\text{CuS}_2}$  refer to the energies of Cu<sup>+</sup>, silicalite-2 cluster model, and metal plus silicalite-2, respectively. The absolute values of *BE* will be considered for comparison.

## RESULTS AND DISCUSSION

To probe a relatively less explained aspect of the field, the interactions of Cu<sup>+</sup> ions with a silicalite-2 framework at different sites explored for this material are compared here. The situation addressed in this article represents a group of



**Fig. 2.** The optimized geometries of the main six metal-silicalite-2 clusters in Cu-doped silicalite-2 where the darker atoms refer to lattice oxygen, the plain bigger balls of the framework represent silicon atoms and the terminal white balls indicate saturating hydrogen atoms. The copper atoms have been labeled on each site for clarity.

sites containing either an anion species, such as a hydroxyl group with a -1 charge, or a framework aluminum atom, placed too distantly from the cation in a high-silica ZSM-11 or silicalite-2 lattice. The sites can also represent monovalent ionic molecules of copper studied from a broad comparative point of view. Moreover, the situation examined here can be a representative for an instantaneous intermediate step in a complex mechanism involving anion/cation exchange during the chemical reactions. Although temporary, the present study probes the likelihood of such bindings, indicating quantitatively whether these structures are stable and plausible. Regardless of the anion attached to the cation or somewhere to the surface, therefore, it appears interesting to obtain a deeper insight into the cation-surface interactions for an oxide surface unaddressed computationally so far.

It has been proven experimentally and theoretically that the coordination of metal cations such as copper in zeolites involves an electronic perturbation of the charge distribution over the binding sites where an electron charge transfer from the framework to the metal occurs. The extent of this transfer is correlated well with the formal charge of the ion and the bond distance parameters [49]. Table 1 displays the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of different active sites and their respective HOMO-LUMO gaps after and before the metal loading (with and without Cu incorporation, respectively). In Fig. 2, the optimized geometries of individual metal atoms interacting with the oxide surface are depicted. Assuming an electron accepting behavior from copper ions and electron donating property of the oxide cluster, a higher HOMO level of the support structure implies a higher reactivity of the oxide surface to the metal. As such, the results of Table 1 indicate that the 6MR site M3 has the highest reactivity towards the Cu ions, presenting the only HOMO level above -8 eV, followed by the cage-like C site. This observation corresponds with the coordination states illustrated in Fig. 2, which indicates a fivefold coordination of Cu in M3 site and a fourfold one in C position. In contrast, the I cluster presents lower electron donation strength as predicted from its more stable HOMO energy level.

In circumstances where Cu/silicalite-2 plays the role of an electron donor, a higher HOMO level of Cu-surface is

equivalent to a higher tendency for electron transfer to the LUMO of the guest molecule. In the present case, the M4-Cu structure shows the highest reactivity towards a stronger electron acceptor ligand. On the other hand, the M2-Cu and I-Cu sites are equally less reactive than the other sites (Table 1). These observations are in agreement with the analogous trend reported in the literature in which the electron donation ability of the active site is correlated with the degree of coordination. For example, the Cu centers became stronger electron donors and weaker electron acceptors upon increasing the coordination of metal to O atoms. This in turn results in a greater charge transfer to CO and NO thus leading to increased C-O and N-O bond lengths and their lower stretching frequencies [65,47].

On the contrary, when Cu-surface clusters accept electrons from a strong donor, a lower level of LUMO translates into a faster reaction with the adsorbed molecule. An example of such a strong donor ligand is the ammonia molecule which transfers about 0.3 electrons to the Cu<sup>+</sup> cation, accommodated in the 4s, 4p orbitals, with the 3d subshell being already full [15]. As evident from Table 1, the I-Cu cluster has the lowest LUMO level with  $E_{\text{LUMO}} = -8.00$  eV indicating that the I-Cu site reflects better electron accepting properties on the basis of the frontier molecular orbital (FMO) theory [92] compared to the other sites. In contrast, the M3-Cu center shows less considerable acceptor ability than any other site.

The larger the energy gap between the HOMO and LUMO levels, the harder and more stable or less reactive the molecule [93-96]. A small gap, on the contrary, means high polarizability and global chemical reactivity [97-103]. It is understood from Table 1 that the HOMO-LUMO gap at the DFT level on all-silica ZSM-11 falls into the range of 7.23-7.84 eV which is almost close to the estimated magnitude of 8.3 eV for silica taking (HO)<sub>3</sub>Si-O-Si(OH)<sub>3</sub> cluster as a model of the surface [5]. The HOMO-LUMO gap can also be compared against the experimental values of 8.6-8.8 eV on silica samples [5]. The lower magnitudes obtained here for the HOMO-LUMO gaps of silicalite-2 can indicate [26] the lower stability or the higher reactivity of this silicalite material with respect to the amorphous silica. Moreover, the comparisons of HOMO-LUMO gaps in the absence and the presence of Cu<sup>+</sup> ion can indicate that the incorporation of copper ion has enhanced the reactivity of

**Table 1.** Calculated HOMO and LUMO Levels and HOMO-LUMO Energy Gaps ( $\Delta E_{\text{HOMO-LUMO}}$ ) for the Investigated Sites at B3LYP/6-311+G\* where the -Cu Suffix Implies after Copper Adsorption

Cluster	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E_{\text{HOMO-LUMO}}$ (eV)
I-Cu	-11.81	-8.00	3.80
M1-Cu	-11.67	-7.59	4.07
M2-Cu	-11.82	-6.52	5.30
M3-Cu	-11.01	-5.72	5.30
M4-Cu	-10.96	-6.20	4.76
C-Cu	-11.45	-5.85	5.59
I	-8.61	-0.77	7.84
M1	-8.49	-0.71	7.77
M2	-8.19	-0.56	7.63
M3	-7.82	-0.59	7.23
M4	-8.05	-0.91	7.15
C	-8.11	-0.87	7.24

the silicalite-2 structure. More strictly, the most stable clusters (I and M1) turned into the most reactive sites after copper adsorption. In other words, the addition of  $\text{Cu}^+$  ions to the oxide surface is found to reduce the framework stability. To the best of our knowledge, this role of metal incorporation has not received much attention for the Cu-surface systems in the earlier studies. A reverse argument is meanwhile true for the individual HOMO and LUMO energies which experienced higher stability with incorporation of metal. It is also noteworthy that the extent of stabilization is much larger for the LUMO energy levels.

The calculated bond lengths for all Cu-silicalite-2 structures are listed in Table 2. As can be seen, the minimum  $r(\text{Cu-O})$  value (2.071 Å) belongs to  $\text{Cu-O}_2$  in the C-Cu structure followed by the bond lengths of 2.181 and 2.207 Å, respectively, for the  $r(\text{Cu-O}_1)$  and  $r(\text{Cu-O}_2)$  in the I-Cu site. Despite the minimum length observed for one of the Cu-O bonds in C-Cu site, the other bonds of this site are

quite longer. In contrast, the second and third shortest bonds in I-Cu point to the strongest Cu-O binding observed among the CuS2 clusters. It is also found from the data listed in Table 2 that identical lengths are expected for the  $\text{Cu-O}_1$  and  $\text{Cu-O}_3$  bond pair and also for the  $\text{Cu-O}_2$  and  $\text{Cu-O}_4$  pair in M1-Cu, creating a symmetrical geometry for the CuS2 cluster at the 4MR site. The data give also the same lengths for the  $r(\text{Cu-O}_1) \leftrightarrow r(\text{Cu-O}_3)$  and  $r(\text{Cu-O}_4) \leftrightarrow r(\text{Cu-O}_6)$  pairs in M3-Cu site as well as for the  $r(\text{Cu-O}_2) \leftrightarrow r(\text{Cu-O}_8)$ ,  $r(\text{Cu-O}_2) \leftrightarrow r(\text{Cu-O}_8)$ , and  $r(\text{Cu-O}_2) \leftrightarrow r(\text{Cu-O}_8)$  in M4-Cu site again referring to a geometrical symmetry around the longitudinal axis on the 6MR and 8MR planes. The same symmetry can be identified for the Cu-Si distances in the abovementioned clusters (Table 2). A similar tendency of the Cu ion for symmetrical binding has earlier been noticed in previous reports on  $\text{Cu}^{2+}$  adsorbed into an aluminum-containing MFI structure [36].

Table 3 shows the electronic charges of different atoms

**Table 2.** Copper-framework Atom Bond Lengths Obtained for Different Optimized Cu-silicalite-2 Cluster mMels (Å) at B3LYP/6-31+G\*

Cluster	I-Cu	M1-Cu	M2-Cu	M3-Cu	M4-Cu	C-Cu
Cu-O <sub>1</sub>	2.181	2.392	2.569	2.314	2.157	3.032
Cu-O <sub>2</sub>	2.207	2.913	2.301	2.847	3.044	2.071
Cu-O <sub>3</sub>	-	2.392	2.612	2.314	4.006	2.977
Cu-O <sub>4</sub>	-	2.913	2.528	2.571	3.265	2.602
Cu-O <sub>5</sub>	-	-	2.553	3.278	2.162	2.220
Cu-O <sub>6</sub>	-	-	-	2.571	3.265	2.616
Cu-O <sub>7</sub>	-	-	-	-	4.006	-
Cu-O <sub>8</sub>	-	-	-	-	3.044	-
Cu-Si <sub>1</sub>	2.730	2.910	3.080	2.828	2.944	3.223
Cu-Si <sub>2</sub>	-	2.911	2.836	3.133	2.944	2.942
Cu-Si <sub>3</sub>	-	2.910	3.024	3.133	4.154	2.840
Cu-Si <sub>4</sub>	-	2.910	2.931	2.828	4.272	3.045
Cu-Si <sub>5</sub>	-	-	2.832	3.385	2.908	2.780
Cu-Si <sub>6</sub>	-	-	-	3.385	2.908	2.827
Cu-Si <sub>7</sub>	-	-	-	-	4.272	-
Cu-Si <sub>8</sub>	-	-	-	-	4.154	-

in each CuS2 cluster. In all of the cases, a partial electron transfer from the support to the metal atom was evident. The occurring charge transfer was more pronounced than that expected for alkali metals which have a closed  $p^6$  shell and hence their electron affinity is small. A transition metal cation in this system should indeed react differently from alkaline ions because the framework anion is to transfer some electronic charge to the metal empty  $d$  orbitals [15]. It must be noted that as the  $3d$  orbitals are fully occupied in Cu<sup>+</sup> an opening of the  $d$ -shell on Cu<sup>+</sup> (a  $3d-4s$  hybridization) is inevitable for any charge transfer [20]. Moreover, the calculated partial charges on Cu<sup>+</sup> ions given in the first row correspond to a moderate degree of covalent bonding with the framework and hence pointing to a reduced status of the so-called Cu<sup>+</sup> site [17]. These changes are in general

accordance with the experimental observations referring to the changeable oxidation states in CuS2 clusters [60].

As evident from Table 3, the partial positive charge residing on the Cu ion followed the sequence C-Cu < M4-Cu < M3-Cu < M2-Cu < M1-Cu < I-Cu meaning higher oxidation states of copper in the mentioned order. Whereas the net charge of metal atom attached to the silicalite model in I-Cu site was very close to the formal +1 to acquire a stable  $d^{10}$  orbital closed-shell configuration, the corresponding value of the charge state was significantly lower than one electron on Cu ion in the C-Cu cluster. This implied that the cationic nature of the exchanged ion has increased upon decreasing the number of interacting framework oxygens. It is also clear that the addition of copper ion to the cluster changes the partial charges on the

**Table 3.** NBO Partial Charge of Adsorbed Copper and the Lattice Oxygen Atoms in Different Cu-silicalite-2 Clusters at B3LYP/6-311+G\*

Atom	I-Cu	M1-Cu	M2-Cu	M3-Cu	M4-Cu	C-Cu
Cu	+0.95	+0.83	+0.77	+0.76	+0.74	+0.64
O <sub>1</sub>	-1.31	-1.27	-1.26	-1.30	-1.31	-1.25
O <sub>2</sub>	-1.31	-1.23	-1.31	-1.26	-1.27	-1.32
O <sub>3</sub>	-	-1.27	-1.25	-1.30	-1.28	-1.23
O <sub>4</sub>	-	-1.23	-1.28	-1.27	-1.25	-1.26
O <sub>5</sub>	-	-	-1.27	-1.25	-1.30	-1.29
O <sub>6</sub>	-	-	-	-1.27	-1.25	-1.28
O <sub>7</sub>	-	-	-	-	-1.28	-
O <sub>8</sub>	-	-	-	-	-1.27	-

**Table 4.** Bond Angles in Different Cu-silicalite-2 Clusters (in Degrees) at B3LYP/6-31+G\*

Cluster	Angle		Angle	
	(deg.)		(deg.)	
I-Cu	O <sub>1</sub> -Cu-O <sub>2</sub>	71.55	-	-
M1-Cu	O <sub>1</sub> -Cu-O <sub>3</sub>	97.14	-	-
M2-Cu	O <sub>1</sub> -Cu-O <sub>3</sub>	119.88	O <sub>2</sub> -Cu-O <sub>5</sub>	112.74
M3-Cu	O <sub>1</sub> -Cu-O <sub>4</sub>	147.62	O <sub>3</sub> -Cu-O <sub>6</sub>	147.62
M4-Cu	O <sub>1</sub> -Cu-O <sub>5</sub>	150.00	-	-
C-Cu	O <sub>1</sub> -Cu-O <sub>4</sub>	130.21	O <sub>2</sub> -Cu-O <sub>5</sub>	173.58

adjacent O atoms of the silicate portion of the cluster accordingly.

The observed resemblance in a number of bond lengths in M1-Cu, M3-Cu and M4-Cu structures is interestingly true when electronic charge is concerned. In other words, the identical bond lengths have an equal charge difference of  $\Delta q(\text{Cu-O})$ , not shown in Table 3, which is simply calculated as the net charge of copper ion minus the charge of the related oxygen. It is further observed in this table that the

rising and falling trends of  $\Delta q(\text{Cu-O})$  coincide in all sites except M4-Cu with those in Table 2 for the bond lengths. This indicated that the electronic charge of Cu-O bonds in this system has often been inversely proportional to their bond length. Stronger electrostatic interactions of the positively charged metal ion with the negatively charged surface are indeed expected to reduce the Cu-O distance thus leading to more strongly stabilized metal ions in such active sites. The ion stabilization is due partly to the fact



that the  $3d-4s$  promotions diminish the Pauli repulsion between Cu and O atoms and also the electron-electron repulsions in the  $3d$  orbital [58]. In general, the results obtained here were in good agreement with the previously reported data stating that the more planar copper surroundings, the more covalent bonding, and the lower partial charge obtained for copper [40]. Earlier studies have also revealed that the positive charge of a copper ion shrinks upon adsorption on a zeolite or silica surface due to substantial charge transfers from silanol and siloxy groups to the metal atom [40,32,31].

Table 4 lists a number of important bond angles in the investigated sites. As evident from this table, the O-Cu-O bond angles in the M3-Cu and C-Cu sites are relatively large, indicating that more flattened configurations of the Cu ion is formed at these sites in comparison with the others. Moreover, the angle sizes for O<sub>1</sub>-Cu-O<sub>4</sub> and O<sub>3</sub>-Cu-O<sub>6</sub> bridges in the M3-Cu site are identical (both equal to 147.6°), which indicate more symmetrical arrangement of the Cu ion in this site. This observation leads to the early conclusion that the most favorable siting for the copper atom in this oxide framework would be the M3-Cu position. Also, noteworthy about the Cu sites with a coordination number of 2 is that the O-Cu-O bridge angle in the M4-Cu site is larger than that in the I-Cu cluster (Table 4). This explains why the relatively stable I cluster has undergone a larger change in stability with incorporation of copper (Table 1).

According to the quantum theory of atoms in molecules (QTAIM) [86-87], the chemical bonds and molecular reactivity can be interpreted in terms of electron density  $\rho(r)$  and its corresponding Laplacian  $\nabla^2\rho(r)$  at the bond critical point (BCP). According to this theory,  $\nabla^2\rho(r)$  provides information about the electronic charge in such a way that a positive Laplacian implies local depletion of the interatomic densities and  $\nabla^2\rho(r) < 0$  points to locally concentrated ones. As such, classical covalent bonds (with shared interactions) show negative values of  $\nabla^2\rho_{\text{BCP}} < 0$  with relatively high  $\rho_{\text{BCP}}$  (above 0.2 a.u.) and classical ionic bonds (involving closed-shell interactions) present positive values of  $\nabla^2\rho_{\text{BCP}} > 0$  with magnitudes of  $\rho_{\text{BCP}}$  below 0.10 a.u. [58,87]. The topological properties of the investigated clusters at the BCP have been reported in Table 5 which indicates low electron densities along with positive  $\nabla^2\rho_{\text{BCP}}$  values. This suggests that the

interactions of Cu with oxygen atoms of the framework would be classified as closed-shell electrostatic interactions, which agrees well with the common statement that metal-oxygen interactions are characterized by positive values of  $\nabla^2\rho$  at the BCP [58]. The QTAIM calculations implemented here gave no BCP for the Cu-Si interactions. It is also interesting to note from these data that the trends of the electronic densities and the corresponding Laplacian values were in full agreement with those well-defined of bond length in Table 2. Figure 3 depicts the relationships between the electron density, Laplacian and Cu-O bond length according to Tables 5 and 2. Excellent correlations have been obtained. Similar trends were observed for adsorption of Zn<sup>2+</sup> in the silicalite-2 structure [104]. As such, any shortened Cu-O distance in every cluster is accompanied with an increase in both electron density and its Laplacian at the BCP. More specifically, the similar lengths observed in Table 2 for some pairs of the Cu-O bonds in M1-Cu and M3-Cu which gave also identical charges have shown the same  $\rho_{\text{BCP}}$  and  $\nabla^2\rho_{\text{BCP}}$  values, indicating that the Cu-O interactions have been of the same nature in all sites of the silicalite-2 structure.

Table 6 illustrates the Cu<sup>+</sup> binding energy for different CuS<sub>2</sub> clusters. As evident from this table, the binding energy varies from 36.2 to 69.7 kcal mol<sup>-1</sup> where the highest and the lowest values could be assigned to the M3-Cu and M1-Cu sites, respectively. This indicates that the Cu<sup>+</sup> ions are most strongly bound in 6T rings of the silica surface, in agreement with our previous finding that the 6MR M3 site is the most reactive position to the Cu cation. This finding also resembles the previously published data for the Cu<sup>2+</sup> ions which were found to bind preferably to 6MR sites in Al-containing ZSM-5 structure [36]. Similar findings were also reported for exchanged Cu<sup>+</sup> ions in Al-incorporated faujasite [4]. In contrast, the 4MR and the intersection sites provide looser bindings for the impregnating copper ions.

The Cu binding energies obtained here are close to the exchange energies of 43.0-102.2 kcal mol<sup>-1</sup> for Cu<sup>2+</sup> ions in ZSM-5 [36], but quite smaller than other values reported earlier for copper-exchanged aluminosilicates [16,25,33,37, 59,34,61]. The higher magnitudes reported previously for the copper binding energy can in part be explained by the fact that the binding energy of Cu ions should increase with incorporation of Al atoms [4]. The effect of framework type

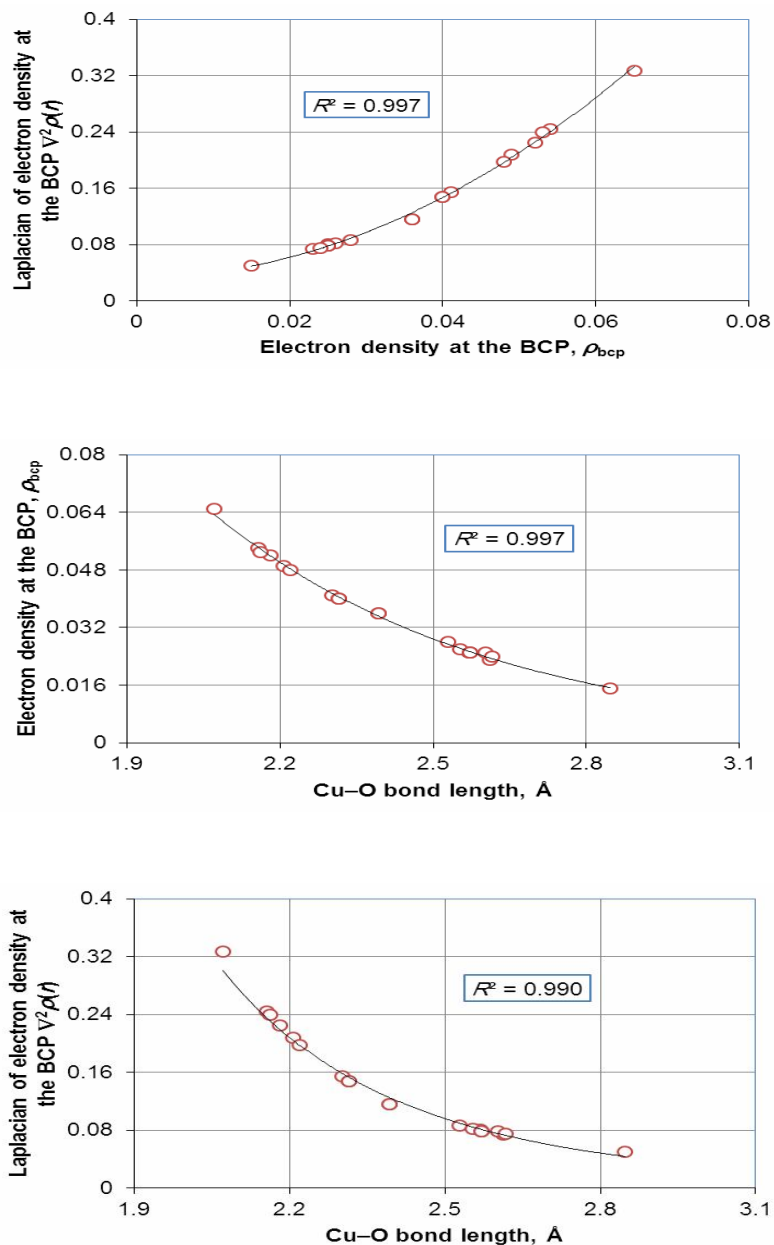
**Table 5.** Topological Properties of the Cu-O Bonds in Different Cu-silicalite-2 Clusters at B3LYP/6-311+G\*

Cluster	I-Cu	M1-Cu	M2-Cu	M3-Cu	M4-Cu	C-Cu
$\rho_{BCP}$						
Cu-O <sub>1</sub>	0.052	0.036	0.025	0.040	0.054	-
Cu-O <sub>2</sub>	0.049	-	0.041	0.015	-	0.065
Cu-O <sub>3</sub>	-	0.036	0.023	0.040	-	-
Cu-O <sub>4</sub>	-	-	0.028	0.025	-	0.025
Cu-O <sub>5</sub>	-	-	0.026	-	0.053	0.048
Cu-O <sub>6</sub>	-	-	-	0.025	-	0.024
$\nabla^2\rho_{BCP}$						
Cu-O <sub>1</sub>	0.225	0.116	0.081	0.148	0.244	-
Cu-O <sub>2</sub>	0.208	-	0.155	0.050	-	0.327
Cu-O <sub>3</sub>	-	0.116	0.074	0.148	-	-
Cu-O <sub>4</sub>	-	-	0.087	0.078	-	0.078
Cu-O <sub>5</sub>	-	-	0.082	-	0.240	0.198
Cu-O <sub>6</sub>	-	-	-	0.078	-	0.075

**Table 6.** Copper Ion Binding Energies (*BE*) Calculated for Cu-silicalite-2 at B3LYP/6-311+G\* (B3LYP/Def2-TZVP) in kcal mol<sup>-1</sup>

Cluster	Population (%)	<i>BE</i>
I-Cu	48	-39.05 (-37.00)
M1-Cu	11	-36.19 (-36.47)
M2-Cu	15	-52.76 (-54.10)
M3-Cu	7	-69.73 (-70.64)
M4-Cu	7	-54.95 (-53.75)
C-Cu	11	-55.79 (-59.66)
Overall <sup>a</sup>	100	-46.07 (-45.72)

<sup>a</sup>Assuming a uniform monolayer coverage.



**Fig. 3.** Correlations observed between the topological and structural properties of the Cu/silicalite-2 cluster models.

and cluster size is probably another source of difference. In previous reports, *e.g.*, the Cu<sup>+</sup> binding energy proved to be dependent upon both the QM cluster size and the Madelung potential [61]. The aliasing effect of the computational method employed is worth attention as well. For example,

while gradient-corrected functionals of BPW91 and BP86 led to larger binding energies in metal/oxide systems, the dependence of the results on the basis set in B3LYP method was not so critical such that a variation of nearly 0.08 eV in binding energy was observed when a triple-zeta basis was

replaced for a double-zeta one [21].

It is of interest to note that although the intersection sites are able to provide favorable bindings for adsorbed molecules, the 6MR M3 sites are more preferred thermodynamically for adsorption of the Cu<sup>+</sup> ions and, then, influence the overall adsorption capacity to higher extents. This difference is more pronounced at low-to-moderate loadings of metal as well explained in the literature [1,4]. At low TMI loadings, *e.g.*, the metal ions were found to opt for exchange sites in six-membered oxygen rings (6MR). Increased TMI loadings diversified the TMI sites, which involve different dimeric and oligomeric species requiring extralattice O atoms (as water, hydroxo and oxo ligands). Removal of these ligands in high-temperature pretreatments leads to an autoreduction property for the TMI, as confirmed by XANES and UV-Vis studies [1]. At moderate loadings of Cu<sup>+</sup> ions where the available sites are uniformly covered as a monolayer adsorption, one may define an overall population-averaged binding energy for the system at hand. The overall value for the Cu-silicalite-2 was found to be -46.07 kcal mol<sup>-1</sup> at the B3LYP/6-311+G\* level (Table 6), which is an indication of a chemisorptions process. As found from the data tabulated, the use of a larger basis set (Def2-TZVP) brings about minor changes in the energy values and no change in the overall trend, with an average binding energy of -45.72 kcal mol<sup>-1</sup>. It is also notable that the C-Cu clusters are not as easily accessible to the guest molecules as the other sites. This means that although relatively stable, the C-Cu sites are practically less important than other high coordination possibilities such as M3 position.

As a complementary note, the lower binding energies obtained here with respect to those on Al-containing MFI zeolites (if can be compared on a sound basis) would in part justify the superior performance of some all-silica zeolites pointed out previously and also the experimentally observed higher sorption power and reactivity of MEL structures in the decomposition of NO molecule. Further works along this line are required to gain more knowledge of the active site behavior for obtaining more detailed mechanistic insights required for design and development of selective catalysts.

## CONCLUSIONS

This paper addressed the coordination and localization of 6 cluster models of Cu<sup>+</sup> in silicalite-2 structure by means of a density functional theory based method in order to analyze the electronic and geometrical properties of metal ion in terms of adsorption/activation properties. The Cu ions were found to predominantly occupy the six-membered ring M3-Cu sites on the walls of the main channels to preferentially form planar symmetry sites with four nearest-neighbor oxygen atoms of the oxide surface. In contrast, the Cu ion is found to be coordinated to only two oxygen atoms at the intersection sites of I-Cu type. As a consequence of strong Cu-O interactions, a charge transfer from the oxide to the adsorbed metal was observed with the following sequence I-Cu < M1-Cu < M2-Cu < M3-Cu < M4-Cu < C-Cu in all-silicate ZSM-11. The Cu-O interactions for the adhesion process were also analyzed from an energetic point of view. As a conclusion, the bond strength of the metal-oxide interactions followed the order M1-Cu < I-Cu < M2-Cu < M4-Cu < C-Cu < M3-Cu as comprehended from the values of binding energy. An opposite relationship was obtained for the trends of data from the electronic charge or the BCP calculations with the metal-oxygen bond lengths. While leading to more stable LUMO and HOMO levels, the incorporation of Cu<sup>+</sup> into the oxide surface intensified the reactivity of the silicalite-2 structure as understood from the HOMO-LUMO gaps. In summary, the results obtained in this investigation were in accordance with most of the previous findings and general trends on similar systems. More specifically, the present findings could explain some interesting data reported previously from kinetic experiments on Cu-silicalite-2 catalysts. A population-averaged value for the binding energy was estimated to be ~46 kcal mol<sup>-1</sup>, which indicates a moderate chemisorption of Cu<sup>+</sup> ions in a Cu/silicalite-2 system.

## REFERENCES

- [1] Smeets, P. J.; Woertink, J. S.; Sels, B. F.; Solomon, E. I.; Schoonheydt, R. A., Transition-metal ions in zeolites: Coordination and activation of oxygen. *Inorg. Chem.* **2010**, *49*, 3573-3583, DOI: 10.1021/ic901814f.

- [2] Delabie, A.; Pierloot, K.; Groothaert, Marijke, H.; Schoonheydt, Robert, A.; Vanquickenborne, Luc G., The coordination of CuII in zeolites-structure and spectroscopic properties. *Eur. J. Inorg. Chem.* **2002**, *2002*, 515-530, DOI: 10.1002/1099-0682(200203)2002:3<515::aid-ejic515>3.0.co;2-6.
- [3] Pidko, E. A.; Hensen, E. J. M.; van Santen, R. A., Self-organization of extraframework cations in zeolites. *Proceedings of the royal society A: Mathematical, Phys. Engin. Sci.* **2012**, *468*, 2070-2086, DOI: 10.1098/rspa.2012.0057.
- [4] Rejmak, P.; Sierka, M.; Sauer, J., Theoretical studies of Cu(i) sites in faujasite and their interaction with carbon monoxide. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5446-5456, DOI: 10.1039/b710051e.
- [5] Lopez, N.; Illas, F.; Pacchioni, G., Adsorption of Cu, Pd, and Cs atoms on regular and defect sites of the SiO<sub>2</sub> surface. *J. Am. Chem. Soc.* **1999**, *121*, 813-821, DOI: 10.1021/ja981753c.
- [6] Jacobs, P. A.; Martens, J. A., *Synthesis of High-Silica Aluminosilicate Zeolites*. Elsevier: 1987.
- [7] Fyfe, C. A.; Gies, H.; Kokotailo, G. T.; Pasztor, C.; Strobl, H.; Cox, D. E., Detailed investigation of the lattice structure of zeolite ZSM-11 by a combination of solid-state NMR and synchrotron x-ray diffraction techniques. *J. Am. Chem. Soc.* **1989**, *111*, 2470-2474, DOI: 10.1021/ja00189a016.
- [8] Čejka, J.; Corma, A.; Zones, S., *Zeolites and Catalysis: Synthesis, Reactions and Applications*. Wiley: 2010.
- [9] Fyfe, C. A.; Lin, Z. S.; Tong, C.; Darton, R. J., Simple, efficient syntheses of zeolite ZSM-11 (MEL) at temperatures below 100 °C using very dense gels. *Micropor. Mesopor. Mat.* **2012**, *150*, 7-13, DOI: 10.1016/j.micromeso.2011.09.021.
- [10] Kustova, M. Y.; Hasselriis, P.; Christensen, C. H., Mesoporous MEL-Type zeolite single crystal catalysts. *Catal. Lett.* **2004**, *96*, 205-211, DOI: 10.1023/B:CATL.0000030122.37779.f4.
- [11] Egeblad, K.; Kustova, M.; Klitgaard, S. K.; Zhu, K.; Christensen, C. H., Mesoporous zeolite and zeotype single crystals synthesized in fluoride media. *Micropor. Mesopor. Mat.* **2007**, *101*, 214-223, DOI: 10.1016/j.micromeso.2006.11.001.
- [12] Chen, H. L.; Ding, J.; Wang, Y. M., One-step synthesis of mesoporous ZSM-11 composites through a dual-template method. *New J. Chem.* **2014**, *38*, 308-316, DOI: 10.1039/c3nj00785e.
- [13] Kustova, M. Y.; Rasmussen, S. B.; Kustov, A. L.; Christensen, C. H., Direct NO decomposition over conventional and mesoporous Cu-ZSM-5 and Cu-ZSM-11 catalysts: Improved performance with hierarchical zeolites. *Appl. Catal. B* **2006**, *67*, 60-67, DOI: 10.1016/j.apcatb.2006.04.014.
- [14] Zhu, J.; Meng, X.; Xiao, F., Mesoporous zeolites as efficient catalysts for oil refining and natural gas conversion. *Front. Chem. Sci. Eng.* **2013**, *7*, 233-248, DOI: 10.1007/s11705-013-1329-2.
- [15] Berthomieu, D.; Krishnamurty, S.; Coq, B.; Delahay, G.; Goursot, A., Theoretical modeling of a copper site in a Cu(II)-Y zeolite. *J. Phys. Chem. B* **2001**, *105*, 1149-1156, DOI: 10.1021/jp002929b.
- [16] Blint, R. J., Copper Coordination in zeolite-supported lean NO<sub>x</sub> catalysts. *J. Phys. Chem.* **1996**, *100*, 19518-19524, DOI: 10.1021/jp9617074.
- [17] Broclawik, E.; Datka, J.; Gil, B.; Kozyra, P., Why Cu<sup>+</sup> in ZSM-5 framework is active in DeNO<sub>x</sub> reaction-quantum chemical calculations and IR studies. *Catal. Today* **2002**, *75*, 353-357, DOI: 10.1016/S0920-5861(02)00063-9.
- [18] Bulánek, R.; Cicmanec, P.; Knotek, P.; Nachtigallova, D.; Nachtigall, P., Localization of Cu<sup>+</sup> sites and framework Al positions in high-silica zeolites: Combined experimental and theoretical study. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2003-2007, DOI: 10.1039/b402950j.
- [19] Davidová, M.; Nachtigallová, D.; Bulánek, R.; Nachtigall, P., Characterization of the Cu<sup>+</sup> sites in high-silica zeolites interacting with the CO molecule: Combined computational and experimental study. *J. Phys. Chem. B* **2003**, *107*, 2327-2332, DOI: 10.1021/jp026989o.
- [20] Davidová, M.; Nachtigallová, D.; Nachtigall, P.; Sauer, J., Nature of the Cu<sup>+</sup>-NO Bond in the Gas phase and at different types of Cu<sup>+</sup> sites in zeolite catalysts. *J. Phys. Chem. B* **2004**, *108*, 13674-13682, DOI: 10.1021/jp0478007.
- [21] Ferullo, R. M.; Castellani, N. J., NCO adsorption over

- SiO<sub>2</sub> and Cu/SiO<sub>2</sub> cluster models from density functional theory. *J. Mol. Catal. A* **2004**, *221*, 155-162, DOI: 10.1016/j.molcata.2004.06.027.
- [22] Ferullo, R. M.; Garda, G. R.; Belelli, P. G.; Branda, M. M.; Castellani, N. J., Deposition of small Cu, Ag and Au particles on reduced SiO<sub>2</sub>. *J. Mol. Struct.* **2006**, *769*, 217-223, DOI: 10.1016/j.theochem.2006.03.048.
- [23] Gao, Y.; Kispert, L. D., A DFT study of the interaction between olefins and Cu<sup>2+</sup> on silica and MCM-41 model surfaces. *Dalton T.* **2014**, *43*, 6221-6228, DOI: 10.1039/c3dt53285b.
- [24] Goodman, B. R.; Hass, K. C.; Schneider, W. F.; Adams, J. B., Cluster model studies of oxygen-bridged Cu pairs in Cu-ZSM-5 catalysts. *J. Phys. Chem. B* **1999**, *103*, 10452-10460, DOI: 10.1021/jp9922110.
- [25] Groothaert, M. H.; Pierloot, K.; Delabie, A.; Schoonheydt, R. A., Identification of Cu(ii) coordination structures in Cu-ZSM-5, based on a DFT/ab initio assignment of the EPR spectra. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2135-2144, DOI: 10.1039/b301120h.
- [26] Hagelberg, F.; Xiao, C.; Lester, W. A., Cagelike Si12 clusters with endohedral Cu, Mo, and W metal atom impurities. *Phys. Rev. B* **2003**, *67*, 035426-035421-035426-035429.
- [27] Hass, K. C.; Schneider, F. W., Density functional studies of adsorbates in Cu-exchanged zeolites: model comparisons and SO<sub>x</sub> binding. *Phys. Chem. Chem. Phys.* **1999**, *1*, 639-648, DOI: 10.1039/a807235c.
- [28] Hass, K. C.; Schneider, W. F., Reliability of small cluster models for Cu-exchanged zeolites. *J. Phys. Chem.* **1996**, *100*, 9292-9301, DOI: 10.1021/jp952702u.
- [29] Kamarudin, K. S. N., Synthesis and Modification of Micro and Mesoporous Materials as CO<sub>2</sub> Adsorbents. 2009, PhD Dissertation, Universiti Teknologi Malaysia.
- [30] Kustova, M. Y.; Kustov, A.; Christiansen, S. E.; Leth, K. T.; Rasmussen, S. B.; Christensen, C. H., Cu-ZSM-5, Cu-ZSM-11, and Cu-ZSM-12 catalysts for direct NO decomposition. *Catal. Commun.* **2006**, *7*, 705-708, DOI: 10.1016/j.catcom.2006.02.019.
- [31] Lopez, N.; Illas, F.; Pacchioni, G., *Ab Initio* theory of metal deposition on SiO<sub>2</sub>. 1. Cun (n = 1-5) clusters on nonbridging oxygen defects. *J. Phys. Chem. B* **1999**, *103*, 1712-1718, DOI: 10.1021/jp9840174.
- [32] Lopez, N.; Pacchioni, G.; Maseras, F.; Illas, F., Hybrid quantum-mechanical and molecular mechanics study of Cu atoms deposition on SiO<sub>2</sub> surface defects. *Chem. Phys. Lett.* **1998**, *294*, 611-618, DOI: 10.1016/S0009-2614(98)00907-5.
- [33] Morpurgo, S.; Moretti, G.; Bossa, M., Basis set effects on Cu(I) coordination in Cu-ZSM-5: a computational study. *Theor. Chem. Acc.* **2012**, *131*, 1-12, DOI: 10.1007/s00214-012-1180-4.
- [34] Nachtigall, P.; Davidová, M.; Nachtigallová, D., Computational study of extraframework Cu<sup>+</sup> sites in ferrierite: Structure, coordination, and photoluminescence spectra. *J. Phys. Chem. B* **2001**, *105*, 3510-3517, DOI: 10.1021/jp002679z.
- [35] Nachtigall, P.; Nachtigallová, D.; Sauer, J., Coordination change of Cu<sup>+</sup> sites in ZSM-5 on excitation in the triplet state: Understanding of the photoluminescence spectra. *J. Phys. Chem. B* **2000**, *104*, 1738-1745, DOI: 10.1021/jp992600u.
- [36] Nachtigallova, D.; Nachtigall, P.; Sauer, J., Coordination of Cu<sup>+</sup> and Cu<sup>2+</sup> ions in ZSM-5 in the vicinity of two framework Al atoms. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1552-1559, DOI: 10.1039/b100712m.
- [37] Nachtigallova, D.; Nachtigall, P.; Sierka, M.; Sauer, J., Coordination and siting of Cu<sup>+</sup> ions in ZSM-5: A combined quantum mechanics/interatomic potential function study. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2019-2026, DOI: 10.1039/a900214f.
- [38] Pidko, E.; Kazansky, V., σ-Type ethane adsorption complexes with Cu<sup>+</sup> ions in Cu(i)-ZSM-5 zeolite. Combined DRIFTS and DFT study. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1939-1944, DOI: 10.1039/b418498j.
- [39] Pierloot, K.; Delabie, A.; Groothaert, M. H.; Schoonheydt, R. A., A reinterpretation of the EPR spectra of Cu(II) in zeolites A, Y and ZK4, based on ab initio cluster model calculations. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2174-2183, DOI: 10.1039/b100531f.

- [40] Pietrzyk, P., Spectroscopy and computations of supported metal adducts. 1. DFT study of CO and NO adsorption and coadsorption on Cu/SiO<sub>2</sub>. *J. Phys. Chem. B* **2005**, *109*, 10291-10303, DOI: 10.1021/jp050842q.
- [41] Ramstad, A. L.; Mikkelsen, Ø., Structural characterisation of copper-containing manganese oxide octahedral molecular sieve (Cu-OMS-2) materials by X-ray absorption spectroscopy and cyclic voltammetry. *J. Mol. Struct.* **2004**, *697*, 109-117, DOI: 10.1016/j.molstruc.2004.04.003.
- [42] Rice, M. J.; Chakraborty, A. K.; Bell, A. T., A density functional theory study of the interactions of H<sub>2</sub>O with H-ZSM-5, Cu-ZSM-5, and Co-ZSM-5. *J. Phys. Chem. A* **1998**, *102*, 7498-7504, DOI: 10.1021/jp981108s.
- [43] Rice, M. J.; Chakraborty, A. K.; Bell, A. T., Theoretical studies of the coordination and stability of divalent cations in ZSM-5. *J. Phys. Chem. B* **2000**, *104*, 9987-9992, DOI: 10.1021/jp0009352.
- [44] Rice, M. J.; Chakraborty, A. K.; Bell, A. T., Site availability and competitive siting of divalent metal cations in ZSM-5. *J. Catal.* **2000**, *194*, 278-285, DOI: 10.1006/jcat.2000.2977.
- [45] Rodriguez-Santiago, L.; Sierka, M.; Branchadell, V.; Sodupe, M.; Sauer, J., Coordination of Cu<sup>+</sup> ions to zeolite frameworks strongly enhances their ability to bind NO<sub>2</sub>. An *ab Initio* density functional study. *J. Am. Chem. Soc.* **1998**, *120*, 1545-1551, DOI: 10.1021/ja973196k.
- [46] Sayle, D. C.; Catlow, C. R. A.; Gale, J. D.; Perrin, M. A.; Nortier, P., Computer modeling of the active-site configurations within the NO decomposition catalyst Cu-ZSM-5. *J. Phys. Chem. A* **1997**, *101*, 3331-3337, DOI: 10.1021/jp963459h.
- [47] Schneider, W. F.; Hass, K. C.; Ramprasad, R.; Adams, J. B., Cluster models of Cu binding and CO and NO adsorption in Cu-exchanged zeolites. *J. Phys. Chem.* **1996**, *100*, 6032-6046, DOI: 10.1021/jp9521924.
- [48] Sierraalta, A.; Bermudez, A.; Rosa-Brussin, M., Density functional study of the interaction of Cu<sup>+</sup> ion-exchanged zeolites with H<sub>2</sub>O and SO<sub>2</sub> molecules. *J. Mol. Catal. A: Chemical* **2005**, *228*, 203-210, DOI: 10.1016/j.molcata.2004.09.037.
- [49] Šponer, J. E.; Sobalík, Z.; Leszczynski, J.; Wichterlová, B., Effect of metal coordination on the charge distribution over the cation binding sites of zeolites. A combined experimental and theoretical study. *J. Phys. Chem. B* **2001**, *105*, 8285-8290, DOI: 10.1021/jp010098j.
- [50] Teraishi, K.; Ishida, M.; Irisawa, J.; Kume, M.; Takahashi, Y.; Nakano, T.; Nakamura, H.; Miyamoto, A., Active site structure of Cu/ZSM-5: Computational study. *J. Phys. Chem. B* **1997**, *101*, 8079-8085, DOI: 10.1021/jp970957x.
- [51] Woertink, J. S.; Smeets, P. J.; Groothaert, M. H.; Vance, M. A.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I., A [Cu<sub>2</sub>O]<sup>2+</sup> core in Cu-ZSM-5, the active site in the oxidation of methane to methanol. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 18908-18913, DOI: 10.1073/pnas.0910461106.
- [52] Solans-Monfort, X., Modelling of adsorption and catalytic processes in H<sup>+</sup> and Cu<sup>+</sup> exchanged ZSM-5 and CHA zeolites. 2003, PhD Dissertation, Universitat Autònoma de Barcelona.
- [53] Sengupta, D.; Adams, J. B.; Schneider, W. F.; Hass, K. C., Theoretical analysis of N<sub>2</sub>O to N<sub>2</sub> conversion during the catalytic decomposition of NO by Cu-zeolites. *Catal. Lett.* **2001**, *74*, 193-199, DOI: 10.1023/a:1016641319587.
- [54] Kim, S. J.; Park, J. W.; Lee, K. Y.; Seo, G.; Song, M. K.; Jeong, S. -Y., Enhanced catalytic performance of copper-exchanged SAPO-34 molecular sieve in methanol-to-olefin reaction. *J. Nanosci. Nanotechnol.* **2010**, *10*, 147-157, DOI: 10.1166/jnn.2010.1506.
- [55] Mitra, S., Preparation and Characterization of Cu-Cr Impregnated Silica Catalyst from Rice Husk. 2014, MSc Thesis, National Institute of Technology.
- [56] Schneider, W. F.; Hass, K. C.; Ramprasad, R.; Adams, J. B., First-principles analysis of elementary steps in the catalytic decomposition of NO by Cu-exchanged zeolites. *J. Phys. Chem. B* **1997**, *101*, 4353-4357, DOI: 10.1021/jp970213j.
- [57] Sengupta, D.; Schneider, W. F.; Hass, K. C.; Adams, J. B., CO oxidation catalyzed by Cu-exchanged zeolites: a density functional theory study. *Catal. Lett.* **1999**, *61*, 179-186, DOI: 10.1023/a:1019053729010.

- [58] Sierraalta, A.; Añez, R.; Brussin, M. -R., Theoretical study of NO<sub>2</sub> adsorption on a transition-metal zeolite model. *J. Catal.* **2002**, *205*, 107-114, DOI: 10.1006/jcat.2001.3425.
- [59] Sung, C. -Y.; Al Hashimi, S.; McCormick, A.; Tsapatsis, M.; Cococcioni, M., Density functional theory study on the adsorption of H<sub>2</sub>S and other claus process tail gas components on copper- and silver-exchanged Y zeolites. *J. Phys. Chem. C* **2011**, *116*, 3561-3575, DOI: 10.1021/jp2097313.
- [60] Tajima, N.; Hashimoto, M.; Toyama, F.; Mahmoud El-Nahas, A.; Hirao, K., A theoretical study on the catalysis of Cu-exchanged zeolite for the decomposition of nitric oxide. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3823-3830, DOI: 10.1039/a903383a.
- [61] Treesukol, P.; Limtrakul, J.; Truong, T. N., Adsorption of nitrogen monoxide and carbon monoxide on copper-exchanged ZSM-5: A cluster and embedded cluster study. *J. Phys. Chem. B* **2001**, *105*, 2421-2428, DOI: 10.1021/jp004280g.
- [62] Ahmed, A. H., First synthesis of zeolite-encapsulated copper(II)hydrazone complex: Characterization and CO adsorption. *J. Appl. Sci. Res.* **2007**, *3*, 1663-1670.
- [63] Yokomichi, Y.; Yamabe, T.; Ohtsuka, H.; Kakumoto, T., Theoretical study of NO decomposition on Cu-ZSM-5 catalyst models using the density functional method. *J. Phys. Chem.* **1996**, *100*, 14424-14429, DOI: 10.1021/jp960403e.
- [64] Schneider, W. F.; Hass, K. C.; Ramprasad, R.; Adams, J. B., Density functional theory study of transformations of nitrogen oxides catalyzed by Cu-exchanged zeolites. *J. Phys. Chem. B* **1998**, *102*, 3692-3705, DOI: 10.1021/jp9734383.
- [65] Ramprasad, R.; Schneider, W. F.; Hass, K. C.; Adams, J. B., Theoretical study of CO and NO vibrational frequencies in Cu-water clusters and implications for Cu-exchanged zeolites. *J. Phys. Chem. B* **1997**, *101*, 1940-1949, DOI: 10.1021/jp961472w.
- [66] Terasaki, O.; Ohsuna, T.; Sakuma, H.; Watanabe, D.; Nakagawa, Y.; Medrud, R. C., Direct observation of "Pure MEL Type" zeolite. *Chem. Mater.* **1996**, *8*, 463-468, DOI: 10.1021/cm950387i.
- [67] Pietrzyk, P.; Piskorz, W.; Sojka, Z.; Broclawik, E., Molecular structure, spin density distribution, and hyperfine coupling constants of the η<sup>1</sup>{CuNO}11 adduct in the ZSM-5 zeolite: DFT calculations and comparison with EPR data. *J. Phys. Chem. B* **2003**, *107*, 6105-6113, DOI: 10.1021/jp034173x.
- [68] Chester, A. W.; Derouane, E. G., Zeolite Characterization and Catalysis: A Tutorial. Springer: 2009.
- [69] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian 98, Revision A.7. Gaussian Inc., Pittsburgh PA: 1998.
- [70] Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988**, *38*, 3098-3100, DOI: 10.1103/PhysRevA.38.3098.
- [71] Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652, DOI: 10.1063/1.464913.
- [72] Lee, C.; Yang, W.; Parr, R. G., Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785-789, DOI: 10.1103/PhysRevB.37.785.
- [73] Yumura, T.; Yamashita, H.; Torigoe, H.; Kobayashi, H.; Kuroda, Y., Site-specific Xe additions into Cu-ZSM-5 zeolite. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2392-2400, DOI: 10.1039/b919032e.
- [74] Hariharan, P. C.; Pople, J. A., Accuracy of AHn equilibrium geometries by single determinant molecular orbital theory. *Mol. Phys.* **1974**, *27*, 209-



- 214, DOI: 10.1080/00268977400100171.
- [75] Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A., Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, *77*, 3654-3665, DOI: 10.1063/1.444267.
- [76] Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R., Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F. *J. Comput. Chem.* **1983**, *4*, 294-301, DOI: 10.1002/jcc.540040303.
- [77] Frisch, M. J.; Pople, J. A.; Binkley, J. S., Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984**, *80*, 3265-3269, DOI: 10.1063/1.447079.
- [78] Kendall, R. A.; Dunning, T. H.; Harrison, R. J., Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796-6806, DOI: 10.1063/1.462569.
- [79] Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305, DOI: 10.1039/b508541a.
- [80] Feller, D., The role of databases in support of computational chemistry calculations. *J. Comput. Chem.* **1996**, *17*, 1571-1586, DOI: 10.1002/(sici)1096-987x(199610)17:13<1571::aid-jcc9>3.0.co;2-p.
- [81] Glendening, E.; Badenhop, J.; Reed, A.; Carpenter, J.; Weinhold, F., NBO 3.1. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI 1996.
- [82] Rodríguez, J. I.; Bader, R. F. W.; Ayers, P. W.; Michel, C.; Götz, A. W.; Bo, C., A high performance grid-based algorithm for computing QTAIM properties. *Chem. Phys. Lett.* **2009**, *472*, 149-152, DOI: 10.1016/j.cplett.2009.02.081.
- [83] Bader, R. F. W., A quantum theory of molecular structure and its applications. *Chem. Rev.* **1991**, *91*, 893-928, DOI: 10.1021/cr00005a013.
- [84] Bader, R. F. W., The quantum mechanical basis of conceptual chemistry. *Monatsh. Chem.* **2005**, *136*, 819-854, DOI: 10.1007/s00706-005-0307-x.
- [85] Bader, R. F. W., Molecular fragments or chemical bonds. *Accounts Chem. Res.* **1975**, *8*, 34-40, DOI: 10.1021/ar50085a005.
- [86] Bader, R. F. W., *Atoms in Molecules: A Quantum Theory*. Oxford University Press: 1994.
- [87] Matta, C. F.; Boyd, R. J., *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*. Wiley-VCH Verlag GmbH & Co. KGaA: 2007.
- [88] Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R., New software for searching the Cambridge Structural Database and visualizing crystal structures. *Acta Crystallogr. B* **2002**, *58*, 389-397, DOI: 10.1107/S0108768102003324.
- [89] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A., Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008**, *41*, 466-470, DOI: 10.1107/S0021889807067908.
- [90] Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J., Mercury: visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39*, 453-457, DOI: 10.1107/S002188980600731X.
- [91] Taylor, R.; Macrae, C. F., Rules governing the crystal packing of mono- and dialcohols. *Acta Crystallogr. B* **2001**, *57*, 815-827, DOI: 10.1107/S010876810101360X.
- [92] Fukui, K.; Yonezawa, T.; Shingu, H., A molecular orbital theory of reactivity in aromatic hydrocarbons. *J. Chem. Phys.* **1952**, *20*, 722-725, DOI: 10.1063/1.1700523.
- [93] Chattaraj, P. K.; Maiti, B., HSAB principle applied to the time evolution of chemical reactions. *J. Am. Chem. Soc.* **2003**, *125*, 2705-2710, DOI: 10.1021/ja0276063.
- [94] Datta, D., On Pearson's HSAB principle. *Inorg. Chem.* **1992**, *31*, 2797-2800, DOI: 10.1021/ic00039a025.

- [95] Ho, T.-L., The Hard soft acids bases (HSAB) principle and organic chemistry. *Chem. Rev.* **1975**, *75*, 1-20, DOI: 10.1021/cr60293a001.
- [96] Parthasarathi, R.; Subramanian, V.; Chattaraj, P. K., Effect of electric field on the global and local reactivity indices. *Chem. Phys. Lett.* **2003**, *382*, 48-56, DOI: 10.1016/j.cplett.2003.09.160.
- [97] Pearson, R. G., Recent advances in the concept of hard and soft acids and bases. *J. Chem. Educ.* **1987**, *64*, 561-567, DOI: 10.1021/ed064p561.
- [98] Parr, R. G.; Szentpály, L. v.; Liu, S., Electrophilicity Index. *J. Am. Chem. Soc.* **1999**, *121*, 1922-1924, DOI: 10.1021/ja983494x.
- [99] Parr, R. G.; Pearson, R. G., Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516, DOI: 10.1021/ja00364a005.
- [100] Parr, R. G.; Weitao, Y., Density-Functional Theory of Atoms and Molecules. Oxford University Press: 1989.
- [101] Vektariene, A.; Vektaris, G.; Svoboda, J., A theoretical approach to the nucleophilic behavior of benzofused thieno[3,2-b]furans using DFT and HF based reactivity descriptors. *ARKIVOC* **2009**, *7*, 311-329, DOI: 10.3998/ark.5550190.0010.730.
- [102] Gopalakrishnan, S. B.; Kalaiarasi, T.; Subramanian, R., Comparative DFT study of phytochemical constituents of the fruits of *cucumis trigonus roxb.* and *cucumis sativus linn.* *J. Comput. Methods Phys.* **2014**, *2014*, 623235-623231-623235-623236, DOI: 10.1155/2014/623235.
- [103] Aihara, J.-i., Reduced HOMO-LUMO gap as an index of kinetic stability for polycyclic aromatic hydrocarbons. *J. Phys. Chem. A* **1999**, *103*, 7487-7495, DOI: 10.1021/jp990092i.
- [104] Ghashghaee, M.; Ghambarian, M.; Azizi, Z., Characterization of extraframework Zn<sup>2+</sup> cationic sites in silicalite-2: a computational study. *Struct. Chem.* **2016**, *27*, 467-475, DOI: 10.1007/s11224-015-0575-y.