

## Local reactivity index as descriptor of benzene adsorption in cluster models of exchanged zeolite-Y

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### Abstract

The adsorption of benzene over sites I, II and III of Cu- and Na-exchanged zeolite-Y, has been studied using the energy profiles for the host–guest interaction, and electronic descriptors of reactivity such as the electronic chemical potential and a local  $\sigma_k$  index recently defined. Both, the energy and the reactivity index based models consistently complement each other to give a correct interpretation of the reactivity and selectivity patterns experimentally established for these systems.

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### 1. Introduction

Zeolites are crystalline aluminosilicate materials with many industrial applications. Several hydrocarbon transformations are catalyzed by zeolites because their specific and particular acidic and basic properties. For instance, Faujasite (a type of zeolite-Y) is used in the refinery process in which long-chain alkanes are transformed into petroleum derivative products [1–5]. In this particular context, the interaction of the aromatic compounds (such as benzene, which are substrates or intermediates in many catalytic processes) with the zeolite framework constitute a piece of fundamental interest for the understanding and rationalization of global and local aspects of the reactivity of these materials [5–9].

Global reactivity may be conveniently described in terms of global response functions derived in the context of the density functional theory [10]. They are usually expressed as derivatives of the electronic energy,  $E$ , with

respect to the number of electrons  $N$  in the system. For instance, the first derivative of  $E$  with respect to  $N$  describes the electronic chemical potential  $\mu$ . This reactivity index is the natural descriptor of the charge transfer ability of a molecule. During a chemical reaction, the electronic cloud flows from the region of high  $\mu$  value towards the region with minimum  $\mu$  value, until a regime of unique electronic chemical potential (i.e., electronegativity equalization) is attained at equilibrium over the whole molecular interacting system. The derivative of  $\mu$  with respect to  $N$  describes the global hardness  $\eta$  of the system, a quantity related to the resistance of the system to exchange electronic charge with the environment. The inverse of chemical hardness defines the chemical softness  $S = 1/\eta$ , a quantity related to the electronic polarizability of molecules. All these global descriptors of reactivity have been given operational definitions in terms of the vertical ionization potential,  $I$  and electron affinity,  $A$  [11–13]. A current approximation is to use Koopmans' theorem to express these quantities in terms of the frontier one electron energy levels HOMO and LUMO [14–16].

Besides the global quantities, it has been also possible to define local reactivity indexes that conveniently describe those sites where the reactivity pattern dictated

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by the global quantities is developed. These reactivity indexes are directly concerned with the selectivity of the molecule towards specific chemical events. The most relevant local descriptor of reactivity is the Fukui function  $f(\mathbf{r})$ , the derivative of the electronic chemical potential with respect to the external potential due to the compensating nuclear charges in the system [10]. This local index may be further cast into the derivative of the electron density with respect to the number of electrons through a Maxwell relationship. The Fukui function of the system defines the more reactive regions in a molecule. The local softness  $s(\mathbf{r}) = f(\mathbf{r})S$ , is also a useful local descriptor of reactivity incorporating the effect of the global softness,  $S$ . An exhaustive review of the subject has recently been published [17].

The set of global and local response functions have played a key role in describing the reactivity and selectivity of molecules in a wide diversity of situations [18–20]. However, when applied to extended systems, the evaluation of global and local quantities becomes difficult, as the electronic structure of these materials display a band like structure at both the occupied (valence band) and unoccupied (conduction band) states rather than a discrete electronic structure [21,22].

Recently, we have defined a new local index  $\sigma_k$  through the density of states (DOSs) which describes the basicity of exchanged zeolites [22]

$$\sigma_k = \frac{\int_{\text{VB}} g(E)_k dE}{\int_{\text{VB}} g(E) dE} S, \quad (1)$$

where  $g(E)$  and  $g(E)_k$  are associated with the total and condensed density of states, respectively, and  $S$  with the global softness of the system.

To obtain  $g(E)$ , we replace the discrete eigenstates ( $\varepsilon_i$ ) with a normalized Gaussian function, yielding a model for the DOS through the following function:

$$g(E) = \frac{1}{\Delta\sqrt{\pi}} \sum_i \exp \left[ - \left( \frac{E - \varepsilon_i}{\Delta} \right)^2 \right], \quad (2)$$

where  $\Delta$  is the width of the Gaussian function. This parameter is typically taken as 0.5 eV. The local or condensed DOS is obtained by

$$g(E)_k = \frac{1}{\Delta\sqrt{\pi}} \sum_i P_{ki} \exp \left[ - \left( \frac{E - \varepsilon_i}{\Delta} \right)^2 \right], \quad (3)$$

where  $P_{ki}$  is the atomic population at orbital  $\varepsilon_i$ . This population analysis can be obtained from the model of frontier molecular orbital theory in a frozen orbital approximation [14–16], but extended to all occupied molecular orbitals. In this way,  $\sigma_k$  contains information about the electron density or population associated to the different centers in chemical species. This index takes into account contributions from the Fermi level and the electronic levels close to it. It also describes the electron population at the center  $k$ .

The reliability of the  $\sigma_k$  index as a reactivity descriptor has been extensively discussed in a previous work [22]. It is important to mention that for systems with an energy gap at the Fermi level, like the cluster models of zeolites, the reactivity indexes should be defined as derivatives from above or from below. In the case of the electron-donor systems, like the zeolites, the derivatives are taken from below. This is the reason of using information of the orbitals around the HOMO in the construction of  $\sigma_k$ . If a model based on the DOS is successful in explaining the reactivity of a small model of the zeolite, it will be surely good for more extended systems. However, it is important to note, that the index  $\sigma_k$  could be useful for all systems where the reactivity is not only dictated by the HOMO but also by other low-energy orbitals independent of the size of the molecule. For metallic systems without a gap, there is no discontinuity in the derivatives and the application of the DOS is more straightforward as demonstrated recently [23].

In order to further explore the global and local reactivity of the complex zeolite system using reactivity indexes derived from the DOS, we focused in this work on the benzene adsorption at the different sites of exchanged zeolites-Y, which have been simulated by cluster models.

## 2. Computational details

Site models of zeolites were cut from the crystalline structure of Faujasite [7,9] and they have been used in this

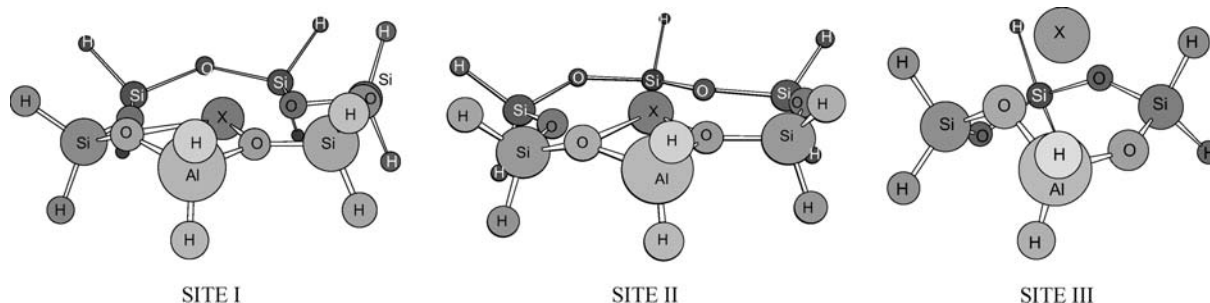


Fig. 1. Model clusters of six- and four-membered ring with exchanged cation ( $X = \text{Cu}$  and  $\text{Na}$ ).

work as the input structure. For sites I (SI) and II (SII) a six-membered ring model cluster was chosen. For site III (SIII) a four-membered ring model cluster was employed. These models have a Si/Al ratio of 5 and 3, for the six- and four-membered rings, respectively. The dangling bonds were saturated with hydrogen atoms. The resulting clusters are shown in Fig. 1. The geometry of all clusters were optimized (with and without the cationic impurity) keeping the positions of Si, Al and the dangling bond atoms, fixed. The benzene was optimized in isolated form and adsorbed over the exchanged cluster models. The complex cluster–benzene was optimized keeping the individual geometries fixed, and optimizing the approach of the molecule toward the different models. The calculations were performed using GAUSSIAN 98 [24] software at the B3LYP [25–27] level of theory, using the Stuttgart pseudo-potential with the corresponding basis set [28,29]. The local indexes  $\sigma_k$  for the cluster models of the exchanged zeolite were calculated using Eq. (1).

### 3. Results and discussion

The energy, global softness, and electronic chemical potential,  $\mu$ , of the different systems with the benzene molecule adsorbed on the Cu-exchanged sites are reported in Table 1. According to the  $S$  values and the hard and soft acid and bases (HSABs) principle, which predicts that the interaction between species with similar hardness (or softness) is favored [30–32], we obtain that the order of Cu exchange is  $SI \sim SII \gg SIII$ . Note that this result is also consistent with the electronic chemical potential values quoted in Table 1. The ionic exchange energy (EE) was calculated as the difference between energy of cation exchanged zeolite minus the energies of the free cation and cluster model of zeolite. In Table 2, The EE quantity shows that the exchange is similar at SI and SII; and that SIII is less favored. This result is in agreement with the experimental data, which predict a low cation exchange at site III of zeolite-Y.

Table 1  
Energy and global parameters of benzene, Cu-exchanged sites and complex of benzene adsorbed in Cu-exchanged cluster models

	Energy (a.u.)	$S$	$\mu$
Site I	–125.17276	10.42	0.004
Site II	–125.18332	10.3	0.006
Site III	–82.87103	8.64	0.023
Cu <sup>+</sup>	–197.01745	11.82	–0.493
CuI	–322.49960	11.49	–0.137
CuII	–322.50826	11.35	–0.135
CuIII	–280.13899	14.98	–0.178
Benzene	–37.59908	7.89	–0.124
Benzene–CuI	–360.09916	10.97	–0.132
Benzene–CuII	–360.11113	10.96	–0.131
Benzene–CuIII	–317.75196	11.38	–0.136

Table 2  
Energy of Cu exchanged and benzene adsorption at the sites of zeolite

	Site I	Site II	Site III
Cu-exchange energy (kcal)	–194.14	–192.95	–157.20
Adsorption energy (kcal)	–0.30	–2.38	–8.72

The benzene adsorption shows a similar pattern. The  $S$  gap (calculated as the  $S$  difference between exchanged cluster and benzene) is minimum between benzene and Cu exchanged in SII (CuII). This result suggests a preferential interaction of benzene with the CuII cluster. The  $\mu$  gap between benzene and CuII is very close to that obtained with CuI. This parameter does not clearly describe the differences in adsorption at both exchanged sites. On the other hand, the adsorption energy (AE), calculated as the difference of the energies between the complex benzene–cation exchanged cluster and the free components of the complex, predicts the preferential site of adsorption at CuIII, which is not in agreement with the experiment. However, it is important to remark that the Cu exchange occurs before the benzene adsorption takes place and that this process is the less favored at CuIII. Thus, it is clear that the adsorption at this site does not occur in the absence of cationic exchange. There is not a clear difference between the AE in CuI and CuII and then it is very difficult to explain the preferential selectivity in CuII on the basis of energy arguments alone.

However, selectivity may be more consistently described using local or regional quantities. Table 3 reports the  $\sigma_k$  values obtained with the different Cu-exchanged sites. The description of the framework is similar to that obtained in our previous work concerning the basicity of alkaline-exchanged zeolites [22]. Among the different sites, the oxygen atoms have the highest  $\sigma_k$  values which indicate that the density of oxygen atom is higher than the other framework atoms (Al and Si). When we compare the  $\sigma_{Cu}$  values for the three exchanged sites, we observe that the CuII has the lowest value and the CuIII the highest one. This fact is

Table 3  
 $\sigma_k$  Index of Cu exchanged at the I, II and III sites of zeolite

	CuI	CuII	CuIII
Si	0.47	0.46	0.77
Si	0.39	0.38	0.71
Si	0.47	0.45	0.78
Si	0.40	0.39	
Al	0.47	0.45	0.75
O	1.00	1.00	
O	1.06	1.05	1.81
O	1.20	1.17	1.93
O	0.99	1.00	1.84
O	0.95	0.99	
O	1.23	1.21	2.01
Cu	2.48	2.41	4.38

in agreement with the definition of  $\sigma_k$  previously reported. The greater the  $\sigma_k$  value, the greater is the electronic density at site  $k$ , and the lower the  $\sigma_k$  value, the lower is the electronic density at the site. According to this definition, the Cu cation in SII has the lowest electronic density and therefore its interaction with benzene (an electron donating group) will be favored when compared with the cation in SI and SIII. In this way  $\sigma_k$  is a good tool to predict the electronic deficiency at chemical center and it can be used to predict the interaction between species presenting a band structure.

The abnormally high  $\sigma$  value at the Cu site is somehow striking, as this outcome is not consistent with the known basicity of zeolites, which is normally associated with the oxygen atom. We believe that the capacity of back donation of Cu increases the  $\sigma$  value, and generates this ambiguity. To clarify this aspect, we have also studied the Na-exchanged zeolite, where the electron back donating effect is not present. The results of the optimized Na-exchanged systems and benzene adsorbed on it are reported in Table 4. Benzene and NaII does not show a  $\mu$  gap, thereby indicating that the adsorption at this site is preferential with respect to NaI and NaIII, respectively. From the EE data in Table 5, we may conclude that the Na exchange in SII is favored by about 13 and 30 kcal with respect to SI and SIII, respectively. The AE predict a similar adsorption for NaI and NaII. This wrong energetic result can be traced to the use of cluster models, where SI and SII were simulated by a six-membered ring which do not include the steric effects of these sites in the zeolite-Y framework. The limitation of energetic studies of adsorption associated to the cluster can be again clarified by making a local electronic study using the regional  $\sigma_k$  reactivity index.

In Table 6, the  $\sigma$  values for all atoms of the three Na-exchanged clusters are reported. The oxygen atoms consistently show the highest  $\sigma$  values in each system (the oxygen atom bonded to cation have the highest values),

Table 4  
Energy and global parameters of benzene, Na-exchanged sites and complex of benzene adsorbed in Na-exchanged cluster models

	Energy (a.u.)	S	$\mu$
Benzene	-37.59908	7.89	-0.124
NaI	-125.38090	11.32	-0.130
NaII	-125.41215	10.58	-0.125
NaIII	-83.05460	10.46	-0.145
Benzene–NaI	-162.99219	10.75	-0.126
Benzene–NaII	-163.02171	10.07	-0.120
Benzene–NaIII	-120.67019	11.00	-0.142

Table 5  
Na exchange and benzene adsorption energy of exchanged sites

	Site I	Site II	Site III
Na exchange energy (kcal)	-130.6	-143.59	-115.19
Adsorption energy (kcal)	-7.66	-6.58	-10.36

Table 6  
 $\sigma_k$  Index of Na exchanged at the I, II and III sites of zeolite

	NaI	NaII	NaIII
Si	0.57	0.52	0.72
Si	0.46	0.44	0.68
Si	0.58	0.54	0.71
Si	0.49	0.46	
Si	0.49	0.46	
Al	0.58	0.53	0.67
O	1.25	1.18	
O	1.31	1.22	1.82
O	1.49	1.39	1.97
O	1.30	1.23	1.81
O	1.22	1.17	
O	1.54	1.42	1.98
Na	0.05	0.03	0.10

and therefore they become the basic sites of the zeolite framework. On the other hand, the cation has the lowest  $\sigma$  values, and therefore, it can be associated with the electron deficiency responsible for the acidic properties of the zeolite. This pattern is similar in the all three Na-exchanged systems. Furthermore, from the  $\sigma_{\text{Na}}$  data in the exchanged clusters, we can see that the  $\sigma$  value increase in the order NaII < NaI < NaIII. This indicates a low electron density at the Na center of SII, thereby predicting a favorable interaction with benzene electron cloud.

#### 4. Concluding remarks

In this work, we have tested the reliability of the recently defined  $\sigma_k$  index in the context of the adsorption and interaction of several exchanged zeolites-Y with electron donating species like benzene. This index provides quantitative basis for a clear description of the reactivity of the different sites of zeolite and does not have a direct dependence on the model used, as it is the case of the energy based models, which are very sensitivity to the size of cluster.

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