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QUANTUM-CHEMICAL CALCULATION OF MODIFIED SILICON-CONTAINED ZEOLITE CLUSTERS ELECTRONIC STRUCTURE BY ZINC AND CALCIUM IONS

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Abstract. Geometrical and electronic structure of clinoptilolite clusters modified by zinc and calcium cations were calculated by semiempirical quantum-chemical method PM6. The value of formation heat, potentials of ionization, E_{HOMO} and E_{LUMO} energies, cations and oxygen atoms charges, and also binding energy of cations with the cluster were obtained. The redistribution of electronic density on the oxygen atoms of clusters during formation of bonds with zinc and calcium cations was analyzed. The ability of modified clinoptilolite clusters to sorb the hydrogen ions has been estimated. It has been established that clinoptilolite clusters modified by calcium cations can inhibit corrosive processes on the metals surface.

Keywords: quantum chemical approach, clinoptilolite cluster, electronic density, zinc and calcium cations, electronic structure.

1. Introduction

Natural zeolites, in particular clinoptilolite, are widely used in industry for many chemical and petro-chemical processes as catalysts for various reactions or sorbents for the separation of liquid and gas mixtures [1, 2]. At the same time, great attention is paid to ion-exchange properties of clinoptilolite with participation of alkali, alkaline earth and transition metal ions [3]. The ability of zeolites to exchange with ions without destroying the original material crystal structure is caused by the weak ionic bonds between exchange cations and alumino siliciclastic oxygen core. In addition, the presence of opened cavities and wide channels, where exchange cations are located, assists to reduce ion exchange flow reactions even at low temperatures. The results of the experimental studies of clinoptilolite ion-exchange properties [4-6] demonstrate a pronounced selectivity to large one- and two charged metal cations that is caused mainly by the aspect ratio between exchanging cations and the cavities size in the zeolite structure. Such zeolite properties make them perspective for their usage as inhibiting pigments for organic (anti)corrosion coating fillers. Modified zeolites in which ion exchange positions are occupied by zinc, calcium or magnesium cations, exhibit better inhibiting properties as compared with natural ones [7, 8]. There is evidence [9] that such modified zeolites can increase the effects of other corrosion inhibitors, such as zinc-and calcium-containing phosphate.

From the viewpoint of the matter electron theory [10], zeolite modification by various cations leads to changes of adsorption centers nature, which are reflected in changes of their charge or electron-donor properties. Adsorbed cations on zeolite may also change its geometrical structure and electronic properties – dipole moment, total energy, energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Indicated parameters characterize the reactionary ability and adsorption properties of modified zeolites.

Methods of quantum chemistry in combination with cluster approach are primarily used for the analysis of the material electronic structure. The literature data [11-13] show that methods of quantum chemistry are a powerful tool for calculating the zeolite electronic structure in order to predict their properties including ion-exchanging.

2. Method of Modeling and Calculation

The electronic and geometric structures of the clinoptilolite type zeolites that belong to the class of micro-porous core alumino-silicate, and the exchange cations of alkali or alkaline-earth metal and water molecules located in intra-crystallite space were calculated. According to X-ray

studies [14] clinoptilolite lattice parameters are following: $a = 17.662$ Å; $b = 17.911$ Å; $c = 7.407$ Å. The structure consisting of silicon and oxygen atoms with cations of zinc, calcium and hydrogen adsorbed on their surface was studied in order to simplify calculations. It was experimentally established [15] that the clinoptilolite core structure is built from connected tetrahedral nodes, in which small atoms (called T-atoms) are located in the tetrahedral centers and oxygen atoms – on their tops. T-positions in clinoptilolite are presented preferably by Al and Si atoms. One- and two charged cations Na, Ca, K, Mg and Ba are performing the major ions role in the natural zeolites cavities. The content of the mentioned cations depends on the geochemical mineral formation medium composition and the elements distribution between crystallized minerals. The number of oxygen atoms in the core should be twice more than T-atoms number, because each top relates to two tetrahedron.

The fragment of zeolite structure – $Ze(SiO_2)_{116}$ cluster (Fig. 1) containing 116 atoms (40 silicon atoms and 76 oxygen atoms), was selected for simulation. The electronic and geometric cluster structures were simulated by semi-empirical method PM6 [12] using the MOPAC2009 program [13]. Geometry optimization was performed without including elements of symmetry for all cluster atoms. The full energy of clusters, formation heat, HOMO and LUMO energy, ionization potential of the cluster and the atomic charges were calculated (Table 1). The smaller $Ze(SiO_2)_{30}$ clusters containing 10 silicon and 20 oxygen atoms were calculated as well. The stable structures of $Ze(SiO_2)_{116}$ and $Ze(SiO_2)_{30}$ clusters were obtained after geometrical parameters optimization and the distortion of geometry was not observed. In particular, the cavity with the diameter of about 1 nm typical of real zeolites is present in the 116-atomic cluster.

The calculated geometrical parameters, that are 90–95 % identical to the experimental values, characterize the adequacy of the chosen cluster models. Thus, the calculated Si–O distance for external bonds is 1.6 Å on average, while the experimental distance does not exceed 1.63 Å, according to different sources [1, 15]. There is a little variation in the values of the calculated angles for Si–O–Si and O–Si–O. Thus, the angle for different triples of Si–O–Si atoms is 130–136° (experimental value is 132°) for $Ze(SiO_2)_{30}$ cluster and for triples of O–Si–O atoms – 108–112° (experiment one – 108°).
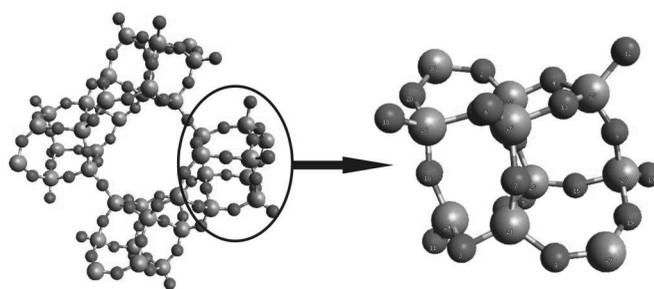

Fig. 1. The structure of 116- and 30-atoms clinoptilolite clusters

The comparison results of the calculated Si–O distances for different $Ze(SiO_2)_{116}$ and $Ze(SiO_2)_{30}$ clusters show a little difference in their values (Table 2). So, there is no significant geometry distortion and change of inter-atomic distances for the decreased cluster. The distribution of charges on the oxygen atoms in these clusters shows a slight deviation in their values for different oxygen atoms (Table 3), that indicates the adequacy of the selected clusters. So, $Ze(SiO_2)_{30}$ cluster was used to reduce the calculation time.

Table 1

The calculated electronic properties of zeolites clusters

Cluster	H, kJ/mol	$-E_{tot}$, eV	I, eV	E_{HOMO}, eV	E_{LUMO}, eV	Δ, eV	m, D
$Ze(SiO_2)_{116}$	-24306.61	25195.02	6.53	-6.84	-2.79	4.05	5.12
$Ze(SiO_2)_{30}$	-5637.10	6583.91	9.19	-9.20	-4.02	5.18	2.69

Notes: H – formation heat; E_{tot} – total energy; I – ionization potential; E_{HOMO} – the highest occupied molecular orbital energy; E_{LUMO} – the lowest unoccupied molecular orbital energy; Δ – energy gap, m – dipole moment

Table 2

The calculated distances (Å) for zeolite clusters

Cluster	Si_{21}–O_1	Si_{21}–O_3	Si_{24}–O_{11}	Si_{27}–O_{17}	Si_{29}–O_{19}
$Ze(SiO_2)_{116}$	1.5887	1.6451	1.3334	1.3465	1.5129
$Ze(SiO_2)_{30}$	1.5234	1.6236	1.3509	1.3587	1.5239

Table 3

The calculated charges of oxygen atoms (a. u.) for zeolite clusters

Cluster	O_1	O_3	O_6	O_{11}	O_{15}	O_{17}	O_{19}
$Ze(SiO_2)_{116}$	-0.4033	-0.4331	-0.3501	-0.3360	-0.3840	-0.3414	-0.3241
$Ze(SiO_2)_{30}$	-0.4218	-0.4377	-0.3616	-0.3522	-0.3988	-0.3605	-0.3368

3. Simulation Results

The structures of zeolite $Ze(SiO_2)_{30}$ clusters modified by zinc, calcium and hydrogen cations (Table 4) were calculated. Cations are bonded with surface oxygen atoms, which act as electron donor centers. From one to six different cations were adsorbed. This modification can generally leads to an increase or decrease of unbound oxygen atoms electron properties, and, consequently, to the change of their activity. In particular, it can be expressed in the formation of bonds with the hydrated hydrogen ions which are present in the environment and their content determines the medium acidity. So, electron donor centers of hydrated zeolite can bind hydrogen ions and thus, the acidity of the medium near the metal surface decreases. This contributes to the corrosion processes retardation taking place on the metal surface.
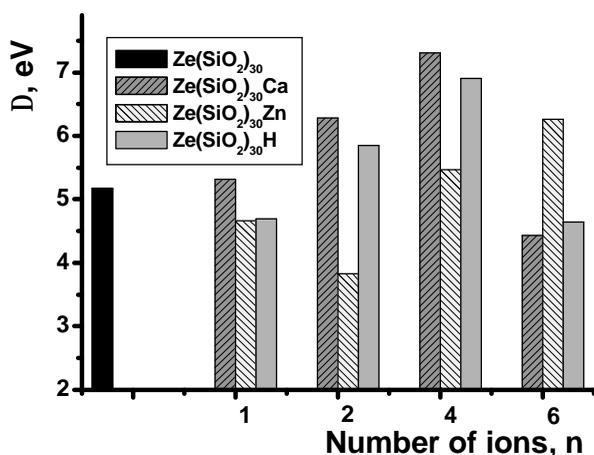

Fig. 2. The dependence of zeolite cluster $Ze(SiO_2)_{30}$ energy gap on ions number and type

Calculations show that these cations significantly influence the stability of zeolite $Ze(SiO_2)_{30}$ clusters. It is observed by the change of the energy gap value Δ (Δ = HOMO-LUMO) on the one hand (Fig. 2), and the significant distortion of the cluster geometry and its structure complete overhaul in some cases – on the other hand. Moreover, clusters stability depends on the number of bound ions. Thus, the increase of calcium ions number on the cluster from one to four increases monotonically the $Ze(SiO_2)_{30}$ stability, while the binding of six calcium ions leads to the significant decrease of the stability and geometry distortion. This indicates the maximum cluster saturation by calcium ions, which does not lead to the structure distortion (Fig. 3). When one or two zinc ions bind with cluster $Ze(SiO_2)_{30}$ the cluster stability decreases. The increased number of bonds with zinc ions increases the cluster stability. Four zinc ions significantly

contribute to the cluster destructing when Si–O bonds are changed (Fig. 4).
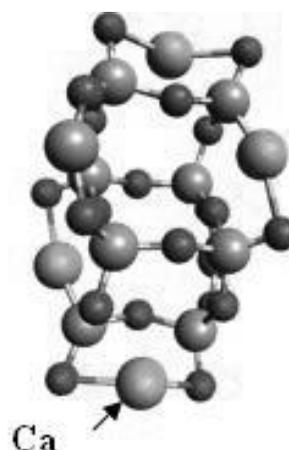
**Fig. 3.** The structure of zeolite cluster $Ze(SiO_2)_{30}$ with 4 calcium ions
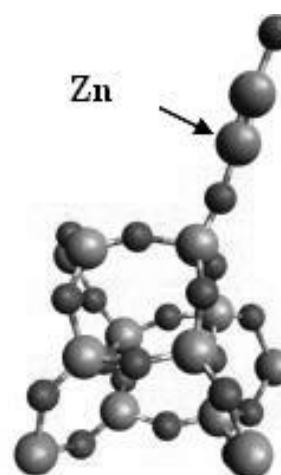
Fig. 4. The structure of zeolite cluster $Ze(SiO_2)_{30}$ with 4 zinc ions

Competing with them hydrogen ions also participate in the ion exchanging on zeolite with various cations in the acidic environment. In general, the interaction of the hydrogen ions with zeolite core oxygen centers leads to the formation of hydroxyl groups and the decrease of zeolite matrix charge, that is connected with decrease of the zeolite sorption capacity of some cations. Our calculations of the hydrogen ions interaction with the zeolite $Ze(SiO_2)_{30}$ cluster indicate a structure stabilization accompanied by symmetry bonds growing until full completion of cluster surface centers by hydrogen ions at the distance of 0.88 Å. In this case, the slight positive charge of about 0.36 a.u. is localized on hydrogen ions. The value is practically unchanged with the increasing number of adsorbed ions.

Evidently, the higher number of adsorbed ions, the higher bond energy of these ions with the zeolite Ze(SiO$_2$)$_{30}$ cluster. It should be noted that zinc ions bond is very strong, that leads to a significant transfer of positive charge to the cluster (about 0.33–0.45 a.u. of charge remain on zinc ion), decrease of Zn–O distance to 1.7–1.9 Å and deformation of the cluster original structure. These facts may indicate that zeolite centers are blocked by zinc ions and lose their ion-exchange properties.

Calcium ions less significantly impact the the structure of the zeolite Ze(SiO$_2$)$_{30}$ original cluster, because their bond energies are lower and interaction distances are 2.1–2.2 Å. However, calcium ions significantly increase the electron density on the free oxygen atoms of Ze(SiO$_2$)$_{30}$ cluster (Table 5).

Presented calculated data indicate the electron donor properties of unbound oxygen atoms during bond formation with calcium, zinc and hydrogen cations. Zinc ions practically do not change the distribution of the electron density on the the cluster oxygen atoms, while calcium ions increase it by 15–50 %. Thus, it is expected that calcium ions will increase the activity of the zeolite cluster centers, promoting not only the sorption of the other metal cations, but the hydrogen ions as well. Consequently, the calculated geometric and electronic properties of zeolite clusters with adsorbed ions suggest that zeolite, clinoptilolite in particular, can significantly affect the properties of the corrosive medium on metal surfaces. Zeolites, that contain the excess of incorporate calcium ions, are more disposed to hydrogen ions sorption and therefore can prevent the penetrating of these ions to the metal surface, retarding the corrosion process.

Activation energies of environment ion interaction with adsorption centers of zeolite clasters are represented in Table 6. Two types of such interaction (adsorption and chemical bonds) for pure and mono-hydrated hydrogen and metal ions (zinc and calcium), as well as 1-, 2- and 4- ions interaction are considered.

Table 4

The calculated electronic characteristic of zeolite clusters with zinc, calcium and hydrogen cations

Zeolite cluster	$-H$, kJ/mol	$-E_{tot}$, eV	I, eV	E_{HOMO}, eV	E_{LUMO}, eV	Δ, eV	q_{Me}, e.u.	E_{bind}, eV	$D_{O\text{-}Me}$, Å
Ze(SiO$_2$)$_{30}$	5637.10	6583.91	9.19	-9.20	-4.02	5.18			
Ze(SiO$_2$)$_{30}$_1Ca	6421.18	6609.70	8.43	-8.43	-3.11	5.32	1.398	0.27	2.284
Ze(SiO$_2$)$_{30}$_2Ca	7326.56	6636.74	8.44	-8.44	-2.16	6.28	1.407	0.55	2.204
Ze(SiO$_2$)$_{30}$_4Ca	8404.44	6683.24	7.79	-7.79	-0.48	7.31	1.341	1.03	2.169
Ze(SiO$_2$)$_{30}$_6Ca	8646.52	6721.07	4.63	-5.34	-0.91	4.43	1.003	1.42	2.245
Ze(SiO$_2$)$_{30}$_1Zn	5721.11	6613.50	8.52	-8.52	-3.86	4.66	0.403	0.58	1.744
Ze(SiO$_2$)$_{30}$_2Zn	5953.83	6644.64	7.87	-7.88	-4.05	3.83	0.325	0.63	1.707
Ze(SiO$_2$)$_{30}$_4Zn	8047.84	6723.79	8.77	-8.77	-3.30	5.47	0.336	1.45	1.995
Ze(SiO$_2$)$_{30}$_6Zn	9702.65	6798.40	8.73	-8.73	-2.47	6.26	0.453	2.22	1.777
Ze(SiO$_2$)$_{30}$_1H	5916.21	6600.31	9.04	-9.04	-4.35	4.69	0.360	0.02	0.889
Ze(SiO$_2$)$_{30}$_2H	6271.14	6617.49	8.66	-8.67	-2.82	5.85	0.360	0.04	0.885
Ze(SiO$_2$)$_{30}$_4H	6830.92	6650.31	8.37	-8.37	-1.47	6.9	0.352	0.07	0.879
Ze(SiO$_2$)$_{30}$_6H	6916.69	6678.21	5.67	-5.67	-1.03	4.64	0.348	0.10	0.875

Notes: q_{Me} – cations Mulliken charge; E_{bind} – bind energy of cations with cluster; $D_{O\text{-}Me}$ – O–Me distance

Table 5

The calculated Mulliken charges on oxygen atoms for zeolite clusters with zinc, calcium and hydrogen cations (e.u.)

Cluster	O$_1$	O$_3$	O$_6$	O$_{11}$	O$_{15}$	O$_{17}$	O$_{19}$
Ze(SiO$_2$)$_{30}$	-0.4218	-0.4377	-0.3616	-0.3522	-0.3988	-0.3605	-0.3368
Ze(SiO$_2$)$_{30}$_4Ca	-0.5082	-0.5262	-0.5716	-0.6721	-0.5720	-0.5941	-0.5238
Ze(SiO$_2$)$_{30}$_4Zn	-0.4454	-0.4278	-0.3967	-0.4357	-0.4098	-0.3780	-0.3567
Ze(SiO$_2$)$_{30}$_4H	-0.4200	-0.4311	-0.3818	-0.4392	-0.3983	-0.4425	-0.4007

**Adsorption activation energies (E_A, eV) and chemical bond formation (E_{bond}, eV)
during interaction between free and monohydrated ion of hydrogen, calcium and zinc with single acidic center of
the zeolite cluster SiO_2 fragment**

	E_A	E_{bond}	$E_{A.\ hydr.}$			$E_{bond\ hydr.}$		
			1 ion	2 ions	4 ions	1 ion	2 ions	4 ions
H^+	0.003	0.017	0.004	0.005	0.006	0.04	0.049	0.054
Ca^{2+}	0.025	0.265	0.069	0.075	0.090	0.449	0.503	0.556
Zn^{2+}	0.047	0.584	0.223	0.265	0.294	0.854	0.957	1.063

In all considered cases the activation energies have low values and favor intensive surface reactions. Hydrogen, calcium and zinc ions exist in hydrated forms in solutions, so their consideration is crucial. The coordination numbers of Ca and Zn are 4 and 6 of water molecules. One can notice the difference in pure and hydrated specimen. Thus calcium and zinc hydrated ions prevail in their interaction with zeolite adsorption centers. Activation energies of zinc are almost four times higher, than those of calcium.

Several times higher activation energies for Zn and Ca compound (relatively to H) leads to prevailing bound of hydrogen ions by zeolite. Taking into account the higher order of bond energies (40–80 kJ/mol), it is evident that Zn and Ca adsorption prevails hydrogen adsorption. In this situation hydrogen ions lost their priority to occupy the constructive metal surfaces. Therefore it should be accepted that full occupation of oxygen adsorption centers by Zn or Ca ions prevents the hydrogen penetration to metal surfaces. Hence one can estimate the amount of zinc or calcium salts to be added to known amount of zeolite in accordance with simple chemical ratio – one functional group of SiO_2 should contain one Ca or Zn ion.

Thus the calculation show that oxygen adsorption centers in zeolite represent active sites with low activation energies, which capture hydrogen ions, zinc and calcium cations. The total occupation of adsorption centers (on elementary fragment of the zeolite structure) leads to the impossibility of hydrogen penetration to metal surface with low activation energies and, as the result, hydrogen can not destruct the constructive metal surface.

4. Conclusions

Quantum-chemical calculation using modern semiempirical molecular orbital method PM6 shows its availability for conducting computer simulations of ion-exchange properties of zeolites with different compositions, that allows to investigate the mechanisms of medium ions interaction with zeolite at atomic-molecular level, and to predict the corrosion processes on the metal surfaces by analyzing electronic characteristics. The effect of increase in electron-donor centers activity of the clusters modified by calcium ions is established *via* the quantum chemical calculations of the structure, electronic and energy characteristics of the clinoptilolite clusters. Their ability to sorb hydrogen ions is established too, which is associated with the formation of stable structures with an excess of calcium ions and increase in the electron density on the unbound oxygen atoms.

References

[1] Auerbach S., Carrado K. and Dutta P.: Handbook of Zeolite Science and Technology. Marcel Dekker Inc., New York 2003.
[2] Rabo J.: Khimiya Zeolitov i Kataliz na Zeolitakh. Mir, Moskwa 1980.
[3] Chelishchev N., Volodin V. and Kryukov V.: Ionoobmennyje Swojstva Prirodnych Vysokokremnistych Zeolitov. Nauka, Moskwa 1988.
[4] Langella A., Pansini M., Cappelletti P. *et al.*: Micropor. Mesopor. Mater, 2000, **37,** 337.
[5] Vasylechko V., Cryshchouk G., Kuz'ma Y. *et al.*: Micropor. Mesopor. Mater, 2003, **60**, 183.
[6] Vasylechko V., Grischuk, G. and Suhnatskyy M.: Visnyk Lviv.Univ., Ser.Khim., 2011, **52,** 148.
[7] Chico B., Simancas J., Vega, J.M. *et al.*: Progr. in Org. Coat., 2008, **61**, 283.
[8] Deflorian F., Fredrizzi L. and Bonora P.: Advances in Corrosion Protection by Organic Coatings III: Proceed. of the Electrochem. Society, 1997, **41-97**, 45.
[9] Ahmed N., Emira H. and Selim M.: Pigment and Resin Techn., 2011, **40,** 91.
[10] Sen K. and Mingos D. (Eds.): Chemical Hardess. Structure and Bonding. Springer, Berlin 1993.
[11] Astala R., Scott M. and Monson P.: J. Phys. Chem. B., 2004, **108**, 9208.
[12] Firsov D., Tolmachev A. and Kryuchenkova N.: Vestnik. Moskowsk. Univ., Ser. 2. Khim., 2010, **1**, 38.
[13] Kubasov A., Kitaev L., Malyshev S. and Novakovskaya Y.: Vestnik. Moskowsk. Univ., Ser. 2. Khim., 2010, **5**, 339.
[14] Korkuna O., Leboda R., Skubiszewska-Zieba J., Vrublevska T. *et al.*: Micropor. and Mesopor. Mat., 2006, **87**, 243.

[15] Breck D.: Zeolitnyje Molekularnyje Syta. Mir, Moskwa 1976.
[16] http://www.iza-structure.org/databases/.
[17] Stewart J.: J. Mol. Model., 2007, **13**, 1173.
[18] Stewart J.: J. Comput. (Aided Mol. Des), 1990, **1**, 1.

КВАНТОВО-ХІМІЧНИЙ РОЗРАХУНОК ЕЛЕКТРОННОЇ СТРУКТУРИ МОДИФІКОВАНИХ КРЕМНІЙВМІСНИХ ЦЕОЛІТНИХ КЛАСТЕРІВ ЙОНАМИ ЦИНКУ І КАЛЬЦІЮ

***Анотація.** Із використанням напівемпіричного квантово-хімічного методу PM6 проведені розрахунки геометричної та електронної структури модифікованих кластерів клиноптилоліту катіонами кальцію та цинку. Отримано значення теплот утворення, потенціалів йонізації, енергій E_{HOMO} та E_{LUMO}, зарядів на катіонах та кислотних центрах, а також енергії зв'язків катіонів з кластером. Проаналізовано перерозподіл електронної густини на атомах кисню кластерів під час утворення зв'язків з катіонами цинку та кальцію. Проведено оцінку реакційної здатності модифікованих кластерів клиноптилоліту до сорбції йонів водню. Втановлено, що модифіковані кластери клиноптилоліту катіонами кальцію можуть сповільнювати корозійні процеси на поверхні металів.*

__Ключові слова:__ квантово-хімічний підхід, кластер клиноптилоліту, електронна густина, катіони цинку і кальцію, електронна структура.