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Molecular modeling of nitrosamines adsorbed on H-ZSM-5 zeolite: An ONIOM study

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Abstract Binding energies of nitrosamine compounds, N-nitrosamine (NA), N-methyl-N-nitrososamine (NMA), N-ethyl-N-nitrososamine (NEA), N,N-dimethyl-N-nitrosoamine (NDMA), N-ethyl-N-methyl-N-nitrosoamine (NEMA) and N,N-diethyl-N-nitrosoamine (NDEA) on the H-ZSM-5 zeolite were obtained using the ONIOM(B3LYP/6–31G(d):AM1) approach. Based on amino and imino isomers of nitrosamines, there are two adsorption configurations on the H-ZSM-5 for NA (as NA_a and NA_i), NMA (as NMA_a and NMA_i) and NEA (as NEA_a and NEA_i). The relative binding energies of nitrosamines are in order: NA_a > NMA_a ~ NEA_a > NA_i > NMA_i ~ NEA_i > NEMA ~ NDEA > NDMA. The order of adsorption selectivity for nitrosamines of the H-ZSM-5 is NA_a ~ NA_i >> NMA_a ~ NEA_a > NDMA ~ NMA_i ~ NEMA > NDEA ~ NEA_i. The selective recognition of the NA by the H-ZSM-5 was obviously found.

Keywords Adsorption · DFT · H-ZSM-5 · Nitrosamines · ONIOM · Selectivity · Zeolite

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Introduction

Nitrosamine compounds are potent carcinogens which are reported by the International Agency for Research on Cancer (IARC) [1]. The nitrosamine can form DNA adduct to cause cancer in the human body [2]. The human can be exposed to the nitrosamines in the environment, including, food and beverage or food processing method such as drying and pan-frying [3–5]. The endogenous formations of nitrosamine compounds in the human body are possible to be one of exposure [4]. Zeolites were one of the adsorbent that were used in the adsorption process. As the zeolites are the aluminosilicate compounds containing the specific size of pore for adsorption process, they can be used for removals of heavy metals [6–8] and nitrosamines. [9–14]. For experimental aspect, the nitrosamine compounds consisting of N,N-dimethyl-N-nitrosoamine (NDMA), N-nitrosopyrrolidine (NPYR) and N-nitrosohexamethyleneimine (NHMI) were adsorbed on zeolite Y, ZSM-5 and A. It was found that the adsorption isotherms were fitted to Freundlich equation. The nitrosamine compounds can be adsorbed on zeolites because of acid-base interaction. The nitrosamine compounds have basic characteristic while the zeolites have acidic characteristic. Moreover, the small size of nitrosamine molecules are adsorbed on zeolites with higher adsorption capacity than the large size of nitrosamine compounds [9]. For calculation aspect, isomers of the gas-phase nitrosamine monomers [15] and dimers [16] were studied using density functional method and the most stable isomer of the monomer has been applied in this work. There were researches of adsorption of nitrosamine compounds by experiment to report the type of adsorption isotherm and kinetic [9, 13]. But it was difficult to determine the complete

structure by the experiment. The computational method can be used to determine with reliable results. In this work, we have investigated the adsorption configurations of the nitrosamine (NA), N-methyl-N-nitrososamine (NMA), N-ethyl-N-nitrososamine (NEA), N,N-dimethyl-N-nitrosoamine (NDMA), N-ethyl-N-methyl-N-nitrosoamine (NEMA) and N,N-diethyl-N-nitrosoamine (NDEA) on the H-ZSM-5 zeolite. The structure optimizations of their adsorption-states have been carried out using the ONIOM(B3LYP/6–31G(d):AM1) approach. The binding energies for the nitrosamines adsorptions on the H-ZSM-5 have been evaluated at the same approach with the zero-point vibration energy (ZPVE) corrections.

Computational details

Geometry optimizations of nitrosamines adsorbed on the H-ZSM-5 modeled as a 50T cluster have been carried out using the hybrid ONIOM methodology [17, 18]. A calculation model of the 50T cluster modeled as a real system of the two-layered ONIOM method with the 5T ($H_3Si(OH)Al(OSiH_3)_2(O)SiH_3$) cluster treated as a high level of theory (see Fig. 1), called as the 50/5T-ONIOM2 model have been employed throughout the work. The dangling bonds at the ends of the 50T cluster model of H-ZSM-5 were saturated with hydrogen atoms. The B3LYP/6–31G(d) [19, 20] and the semiempirical AM1 [21] methods are employed as a high and low levels of theory for the 50/5T-ONIOM2(MO:MO) model. The ONIOM(B3LYP/6–31G(d):AM1) [22–24] have also been employed with the zero-point vibrational energy (ZPVE) corrections. The structure optimizations of isolated species of nitrosamine (NA), N-methyl-N-nitrososamine (NMA), N-ethyl-N-nitrososamine (NEA), N,N-dimethyl-N-nitrosoamine (NDMA), N-ethyl-N-methyl-N-nitrosoamine (NEMA) and N,N-diethyl-N-nitrosoamine (NDEA) computed at the B3LYP/6–31G(d) level and their complexes with 50T-cluster H-ZSM-5 computed at the ONIOM(B3LYP/6–31G(d):AM1) approach ere carried out. As the most stable conformers of amino and imino tautomers of the nitrosamines [15] were considered, two adsorption-complexes of the NA (NA_a and NA_i isomers), NMA (NMA_a and NMA_i isomers) and NEA (NEA_a and NEA_i isomers) were therefore included in the calculations.

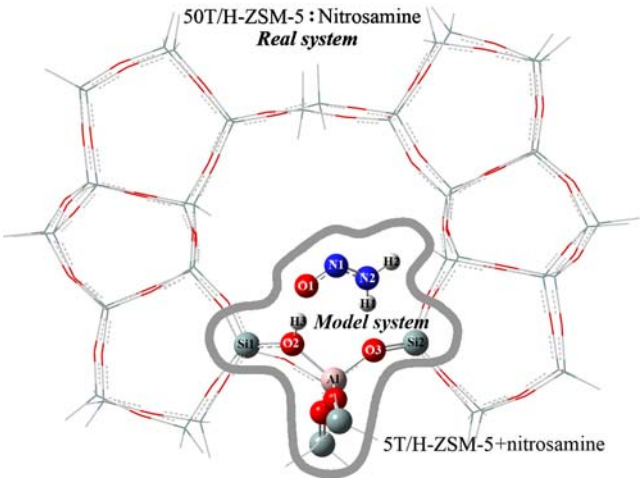

Fig. 1 The 50T cluster model of H-ZSM-5 zeolite for the two-layered ONIOM(B3LYP/6–31G(d):AM1) calculations. The 5T cluster of H-ZSM-5 at the acid site of 10-membered ring is a part of the model system. The ball atoms of the 5T cluster and nitrosamine adsorbate are treated as the high-level layer using at the B3LYP/6–31G(d) level while the rest of the molecular cluster is treated as the low-level layer using at the AM1 theory. The dangling bonds at the ends of the 50T cluster model of H-ZSM-5 were saturated with hydrogen atoms

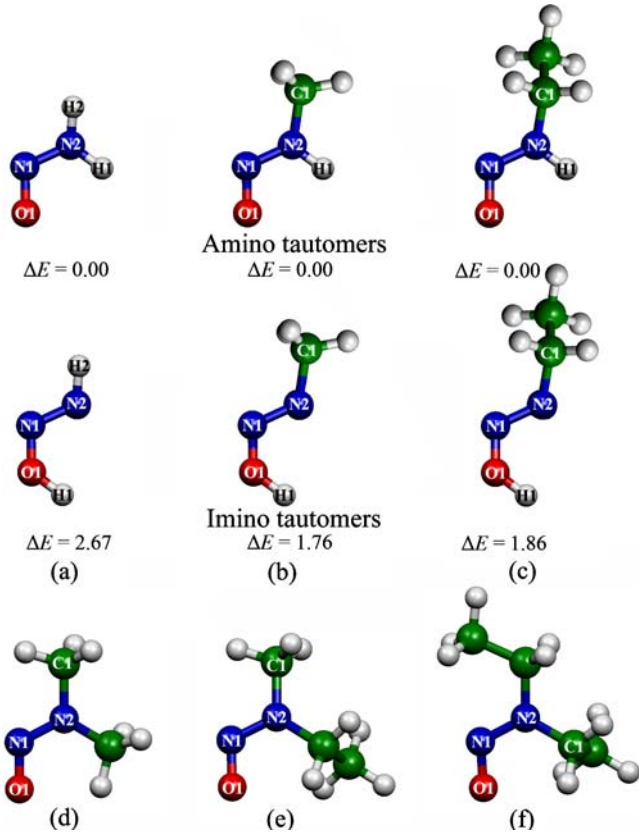

Fig. 2 The B3LYP/6–31G(d) optimized structures of the (**a**) nitrosamine tautomers NA_a (top), NA_i (bottom), (**b**) *N*-methyl-*N*-nitrososamine tautomers NMA_a (top), NMA_i (bottom), (**c**) *N*-ethyl-*N*-nitrososamine NEA_a (top), NEA_i (bottom), (**d**) *N*,*N*-dimethyl-*N*-nitrosoamine (NDMA), (**e**) *N*-ethyl-*N*-methyl-*N*-nitrosoamine (NEMA) and (**f**) N,N-diethyl-N-nitrosoamine (NDEA). The relative energies, ΔE are in kcal mol^{-1}

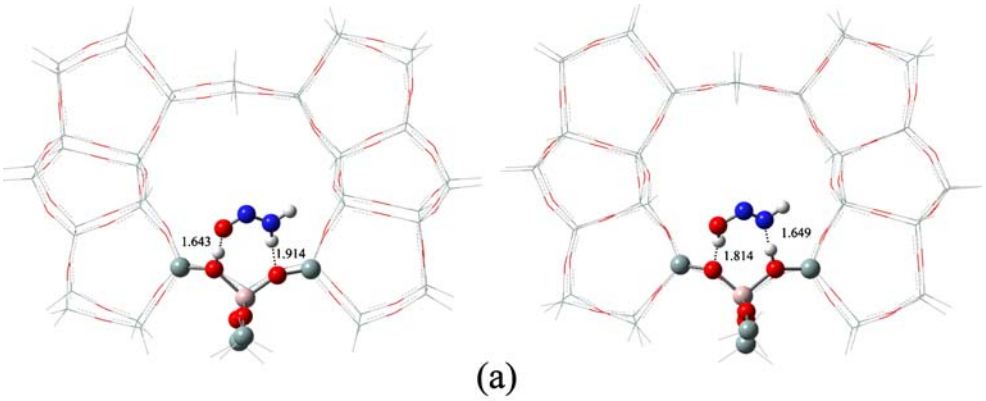

Fig. 3 The ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of adsorption complexes of the H-ZSM-5 zeolite with the (**a**) nitrosamine tautomers NA_a (left), NA_i (right), (**b**) *N*-methyl-*N*-nitrososamine tautomers NMA_a (left), NMA_i (right) and (**c**) *N*-ethyl-*N*-nitrososamine NEA_a (left), NEA_i (right). Hydrogen-bond distance are in angstroms

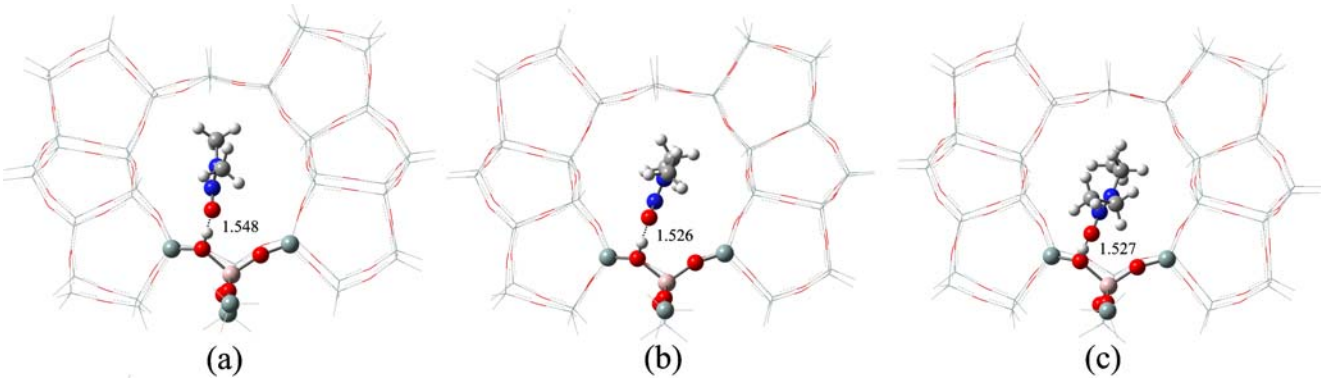

Fig. 4 The ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of adsorption complexes of the H-ZSM-5 zeolite with the (**a**) *N*,*N*-dimethyl-*N*-nitrosoamine (NDMA), (**b**) *N*-ethyl-*N*-methyl-*N*-nitrosoamine (NEMA) and (**c**) N,N-diethyl-N-nitrosoamine (NDEA). Hydrogen-bond distance are in angstroms

Table 1 Selected geometrical data for the isolated and adsorption-state nitrosamines, based on the B3LYP/6–31G(d) level

Parameter	Nitrosamines								
	NA_a	NA_i	NMA_a	NMA_i	NEA_a	NEA_i	NDMA	NEMA	NDEA
Isolated state:									
Bond distance (Å)									
O1-N1	1.221	1.364	1.225	1.374	1.226	1.376	1.225	1.233	1.232
N1-N2	1.339	1.240	1.334	1.237	1.333	1.236	1.347	1.331	1.335
N2-H1	1.010	–	1.021	–	1.022	–	–	–	–
N2-C1	–	–	1.446	1.464	1.453	1.471	1.447	1.464	1.463
O1-H1	–	0.987	–	0.986	–	0.986	–	–	–
Bond angle (°)									
O1-N1-N2	113.6	111.6	113.9	111.6	114.0	111.7	115.9	114.1	115.0
H3-O1-N1	–	105.8	–	105.4	–	105.3	–	–	–
Dihedral angle (°)									
O1-N1-N2-H1	−8.0	–	0.0	–	2.4	–	–	–	–
O1-N1-N2-C1	–	–	180.0	179.7	176.4	179.4	−180.0	−180.0	−178.5
H1-O1-N1-N2	–	0.0	–	0.0	–	0.0	–	–	–
Adsorption state:									
Bond distance (Å)									
O1-N1	1.249	1.335	1.255	1.349	1.257	1.351	1.258	1.262	1.262
N1-N2	1.296	1.248	1.298	1.246	1.297	1.246	1.299	1.292	1.292
N2-H1	1.035	–	1.037	–	1.037	–	–	–	–
N2-C1	–	–	1.455	1.467	1.463	1.474	1.462	1.478	1.476
O1-H1	–	1.007	–	1.003	–	1.002	–	–	–
Bond angle (°)									
O1-N1-N2	115.5	114.7	115.5	114.4	115.5	114.4	113.7	114.0	114.9
H3-O1-N1	–	111.9	–	109.8	–	109.5	–	–	–
Dihedral angle (°)									
O1-N1-N2-H1	−1.0	–	−6.7	–	−5.3	–	–	–	–
O1-N1-N2-C1	–	–	178.0	177.2	175.5	176.0	−177.2	−177.5	−179.3
H1-O1-N1-N2	–	−4.2	–	−17.2	–	−17.9	–	–	–
Adsorbent/H-ZSM-5									
H3···O1	1.643	–	1.577	–	1.570	–	1.548	1.526	1.527
O3···H1	1.914	–	1.979	–	1.974	–	–	–	–
H3···O2	–	1.814	–	1.788	–	1.797	–	–	–
N2···H1	–	1.649	–	1.736	–	1.719	–	–	–
H-ZSM-5									
Bond distance (Å)									
O2-H3	1.018	–	1.027	–	1.029	–	1.030	1.037	1.035
O3-H1	–	1.031	–	1.023	–	1.026	–	–	–
Bond angle (°)									
Si1-O2-Al	133.0	142.6	136.7	148.9	136.5	148.9	133.0	133.3	136.3
O2-Al-O3	101.6	99.1	100.9	98.1	100.9	98.0	104.7	105.3	105.5
Dihedral angle (°)									
Si1-O2-H3···O1	88.8	–	−112.4	–	−99.4	–	163.4	−158.8	−168.8
Si2-O3-H1···N2	–	−178.5	–	−97.1	–	−89.3	–	–	–

Binding energy ($\Delta E_{binding}$), standard enthalpy (ΔH^{o}_{298}) and Gibbs free energy (ΔG^{o}_{298}) of all adsorption of nitrosamines on the H-ZSM-5 have been derived from frequency calculations at the ONIOM(B3LYP/6–31G(d):AM1) level. The adsorption constant (K_{298}) at 298.15 K and 1 atm, is computed using a thermodynamic equation, $\Delta G^{o}_{298} = -RT \ln K$. Binding energy of the nitrosamines adsorbed on the H-ZSM-5 is computed using the following equation.

$$\Delta E_{\text{binding}} = E\left[\text{ONIOM(B3LYP/6-31G(d): AM1)}\right]_{\text{nitrosamine/H-ZSM-5}} - E\left[\text{ONIOM(B3LYP/6-31G(d): AM1)}\right]_{\text{nitrosamine}} - E\left[\text{ONIOM(B3LYP/6-31G(d): AM1)}\right]_{\text{H-ZSM-5}} \quad (1)$$

Table 2 Binding energies, thermodynamics properties, adsorption constants and selectivity coefficients for adsorption processes of nitrosamines to the H-ZSM-5

Adsorbing species[a]	$\Delta E_{binding}$,[b]	ΔH^{o}_{298},[b]	ΔG^{o}_{298},[b]	K_{298}	K_B^{NDEA}
NA_a	−20.78	−19.33	−5.89	2.16×10^{4}	2.30×10^{4}
NA_i	−18.75	−16.87	−4.29	1.44×10^{3}	1.53×10^{4}
NMA_a	−19.86	−16.05	−2.65	8.88×10^{1}	9.46×10^{1}
NMA_i	−18.53	−13.76	−0.53	2.44×10^{0}	2.60×10^{0}
NEA_a	−19.81	−15.39	−1.63	1.59×10^{1}	1.69×10^{1}
NEA_i	−18.52	−13.14	0.21	6.98×10^{-1}	7.43×10^{-1}
NDMA	−16.96	−14.15	−0.92	4.79×10^{0}	5.10×10^{0}
NEMA	−17.90	−13.93	−0.43	2.06×10^{0}	2.19×10^{0}
NDEA	−17.84	−13.41	0.04	9.39×10^{-1}	1.00×10^{0}

[a] For 50/5T cluster model for the H-ZSM-5. [b] In kcal mol^{-1} .

All computations were performed using the Gaussian 03 program package [25]. Binding selectivity of H-ZSM-5 to the nitrosamines with respect to the NDEA derived from the selectivity coefficient (K_B^A) [26] were determined as applied in our previous work. [27]

Results and discussion

Adsorption-state structure

The B3LYP/6–31G(d)-optimized structures of all isolated species of the nitrosamine (NA), N-methyl-N-nitrososamine (NMA), N-ethyl-N-nitrososamine (NEA), N,N-dimethyl-N-nitrosoamine (NDMA), N-ethyl-N-methyl-N-nitrosoamine (NEMA), N,N-diethyl-N-nitrosoamine (NDEA) are shown in Fig. 2. The ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of adsorption complexes of 50T-cluster H-ZSM-5 with nitrosamines NA_a, NA_i, NMA_a, NMA_i, NEA_a and NEA_i shown in Fig. 3 and NDMA, NEMA and NDEA shown in Fig. 4 are obtained. The selected geometrical data for the B3LYP/6–31G(d)-optimized structures of the isolated and adsorption complexes of the studied nitrosamines are given in Table 1. It shows that the O1-N1 bond for amino tautomers of NA, NMA and NEA are slightly longer than their corresponding imino tautomers but the N1-N2 bond for their amino tautomers are shorter than the imino tautomers.

Adsorption complexes of the H-ZSM-5 with nitrosamines are formed via intermolecular hydrogen-bonds and their hydrogen-bond distances are within 1.526 to 1.979 Å as shown in Figs. 3 and 4. The Fig. 3 shows that the NA_a, NMA_a and NEA_a form two hydrogen bonds using their nitroso oxygen and amino hydrogen atoms interacting with hydroxyl hydrogen and silicate oxygen atoms of the H-ZSM-5 zeolite, respectively. On the other hand, the NA_i, NMA_i and NEA_i form two hydrogen bonds using their hydroxyl hydrogen and imino nitrogen atoms interacting with silicate oxygen and hydroxyl hydrogen of the H-ZSM-5 zeolite, respectively. In the case of the adsorption complexes of H-ZSM-5 with NDMA, NEMA and NDEA, only one hydrogen bond is formed via their amino hydrogen atom interacting with the hydroxyl hydrogen atom of H-ZSM-5 zeolite as shown in Fig. 4.

Binding, physical property and selectivity

Binding energies and thermodynamic properties for adsorption processes of all studied nitrosamines to the H-ZSM-5 are given in Table 2. Their binding energies are within a range of −16.96 to −20.78 kcal mol^{-1}. Relative stabilities of the adsorption-state structures based on their relative binding energies are in order: NA_a > NMA_a ~ NEA_a > NA_i > NMA_i ~ NEA_i > NEMA ~ NDEA > NDMA. At 298°C, all adsorption reactions of the studied nitrosamines on the H-ZSM-5 are exothermic process. For the adsorptions at 298°C, all the reaction are spontaneous except that the adsorption of NEA_i and NDEA on the H-ZSM-5 are non-spontaneous process. Adsorption coefficients for these adsorption processes are in order: NA_a ~ NA_i >> NMA_a ~ NEA_a > NDMA ~ NMA_i ~ NEMA > NDEA ~ NEA_i. As the selectivity coefficients of the H-ZSM-5 towards the NA_a and NA_i with respect to NDEA, $K_{NA\_a}^{NDEA} = 2.30 \times 10^4$ and $K_{NA\_i}^{NDEA} = 1.53 \times 10^4$ are fairly high, the selective recognition of the NA by the H-ZSM-5 can therefore be concluded. Nevertheless, the H-ZSM-5 can be used as a gas chromatographic column for separation among these nitrosamine compounds for analytical purpose and for adsorption and storage of the NA as catalyst and environmental purpose.

The preorganization energies and dipole moments for all studied nitrosamines, computed at the B3LYP/6–31G(d) level are given in Table 3. Dipole moments for adsorption-state of the nitrosamines compared to their isolated states are increased except their three imino tautomers, NA_i, NMA_i and NEA_i. The preorganization energies of each structure of the nitrosamine compounds listed in Table 3 are within a narrow range of 1.23 to 2.26 kcal mol^{-1}. It means that very low energy is used to organize the molecular structure of these nitrosamines to form complex with the H-ZSM-5 at the acid site located in its 10-membered ring channel. Size of nitrosamines obviously affect their adsorption configuration aligning in 10-ring channel of the H-ZSM-5; namely the large size as the NDMA, NEMA and NDEA align along the channel of the H-ZSM-5 and only one of their hydrogen bond is formed as shown in Fig. 4.

Table 3 Preorganization energies and dipole moment of nitrosamines, computed at the B3LYP/6–31G(d) level

Nitrosamines	Dipole moment[a]		$E_{isolated}$[b]	$E_{adsorption}$[b]	$\Delta E_{preorg.}$[c]
	Isolated state	Adsorption state			
NA_a	3.60	4.02	−185.84366	−185.84127	1.50
NA_i	1.45	1.25	−185.83939	−185.83688	1.58
NMA_a	3.96	4.34	−225.15824	−225.15558	1.67
NMA_i	2.06	1.84	−225.15542	−225.15182	2.26
NEA_a	4.08	4.48	−264.47518	−264.47242	1.73
NEA_i	2.18	2.00	−264.47221	−264.46843	2.37
NDMA	3.92	4.41	−264.47352	−264.47152	1.25
NEMA	4.12	4.45	−303.78724	−303.78539	1.16
NDEA	4.00	4.34	−343.10334	−343.10135	1.25

[a] In debye. [b] In hartree. [c] In kcal mol^{-1}.

Energy gaps

The lowest unoccupied molecular orbital energies (E_{LUMO}), the highest occupied molecular orbital energies (E_{HOMO}) and frontier molecular orbital energy gaps ($\Delta E_{HOMO\text{-}LUMO}$) of all nitrosamines adsorbed on the H-ZSM-5, based on the ONIOM(B3LYP/6–31G(d):AM1) computations are shown in Table 4. It shows that the relative reactivities of the nitrosamines adsorbed on the H-ZSM-5 are in order: NA_a > NA_i ~ NEA_i ~ NMA_i > NEA_a ~ NMA_a > NDEA > NEMA > NDMA. The NA as either NA_a or NA_i tautomer is the highest values of hardness. Table 4 remarkably shows two groups of two different values of chemical hardness namely a group of nitrosamines two tautomers containing amino and imino functional groups such as NA_a, NA_i, NEA_a, NEA_i, NMA_a and NMA_i of which the values are within a range of 4.706 to 4.898, and a group of nitrosamines containing di-alkyl substituted amino group such as NDEA, NEMA and NDMA of which the values are within a range of 4.488 to 4.597. The electronegativities and chemical potentials of all studied nitrosamines are hardly different.

Table 4 The lowest unoccupied molecular orbital energies (E_{LUMO}), the highest occupied molecular orbital energies (E_{HOMO}), frontier molecular orbital energy gap ($\Delta E_{HOMO\text{-}LUMO}$) and chemical indexes of all nitrosamines adsorbed to the H-ZSM-5, based on the B3LYP/6–31G(d) //ONIOM(B3LYP/6–31G(d):AM1) computations

Adsorbed nitrosamines	E_{LUMO} [a]	E_{HOMO} [a]	$\Delta E_{HOMO\text{-}LUMO}$ [a]
NA_a	−0.163	−9.955	9.792
NA_i	−0.354	−9.982	9.629
NMA_a	−0.435	−9.846	9.411
NMA_i	−0.354	−9.955	9.602
NEA_a	−0.408	−9.846	9.438
NEA_i	−0.326	−9.928	9.602
NDMA	−0.598	−9.574	8.976
NEMA	−0.517	−9.547	9.030
NDEA	−0.408	−9.602	9.194

[a] In eV.

Conclusions

Adsorption complexes of the H-ZSM-5 with the NA, NMA and NEA and with NDMA, NEMA and NDEA are formed with double and single hydrogen bondings, respectively. The NA_a, NMA_a and NEA_a can form two hydrogen bonds using their nitroso oxygen and amino hydrogen atoms interacting with hydroxyl hydrogen and silicate oxygen atoms of the H-ZSM-5 zeolite, respectively. On the other hand, the NA_i, NMA_i and NEA_i form two hydrogen bonds via their hydroxyl hydrogen and imino nitrogen atoms interacting with silicate oxygen and hydroxyl hydrogen atoms of the H-ZSM-5 zeolite, respectively. In the case of the adsorption complexes of the H-ZSM-5 with the NDMA, NEMA and NDEA, only one hydrogen bond is formed via the amino hydrogen atom of these nitrosamines interacting with the hydroxyl hydrogen atom of the H-ZSM-5. Relative stabilities of the adsorption-state structures based on their relative binding energies are in order: NA_a > NMA_a ~ NEA_a > NA_i > NMA_i ~ NEA_i > NEMA ~ NDEA > NDMA. All adsorption processes at 298.15 K are exothermic reaction. Relative reactivities of the nitrosamines adsorbed on the H-ZSM-5 are in decreasing order: NA_a > NA_i ~ NEA_i ~ NMA_i > NEA_a ~ NMA_a > NDEA > NEMA > NDMA. The selectivity coefficients of the H-ZSM-5 toward NA_a and NA_i with respect to the NDEA, $K_{NA\_a}^{NDEA} = 2.30 \times 10^4$ and $K_{NA\_i}^{NDEA} = 1.53 \times 10^4$ are found to be the highest value.

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