THEORETICAL STUDY OF PYRROLE INTERACTION WITH ALKALI METAL EXCHANGED ZEOLITES: INVESTIGATION OF THE RELIABILITY OF CLUSTER AND PERIODIC MODELS

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The interaction of pyrrole with the alkali metal exchanged zeolites was investigated using cluster models of various sizes and with a hybrid quantum mechanics/interatomic potential function model (QM-pot). The interaction of pyrrole with the M^+/zeolite is dominantly driven by the interaction of pyrrole π-system with the alkali metal cation. Further stabilization is due to the formation of the hydrogen bonds between NH and framework oxygen atoms. A good agreement between calculated and experimental shift of the N–H stretching vibration upon the adsorption of pyrrole in M^+/zeolite was found with the periodic QM-pot model. The performance of the cluster models for the description of pyrrole interaction with M^+/zeolite is discussed. Reliable results can be obtained only when large cluster models are used for description of the zeolite framework.
Keywords: Heterogeneous catalysis; Zeolite; ZSM-5; Alkali ions; Probe molecule; Pyrrole; IR; N–H stretching vibrations; Quantum chemistry; QM-pot; DFT; B3-LYP; Core-shell model potential; Cluster models.

Detailed knowledge of the structure and distribution of active sites in various types of zeolite frameworks and an information about the character of the interaction of molecules with the active site are critical for the complete understanding of catalytic properties of zeolites. Methods of computational chemistry can provide some information in this respect, in particular, when information at atomic scale level is required. However, various theoretical models can lead to qualitatively different conclusions, in particular, when the system of interest has as high complexity as active sites in zeolites. It is therefore important to systematically study the performance of various models for the description of active sites in zeolites.

Pyrrole is used as a probe molecule for characterization of basic sites in alkali metal exchanged zeolites[1–5]. Upon the adsorption of pyrrole in alkali metal exchanged zeolite, the IR band corresponding to the N–H stretching

vibration is significantly shifted towards lower energies. The changes can be observed also in NMR spectrum, where the ^{1}H NMR chemical shift of the N–H group changes upon the adsorption[2]. The dependence of the N–H stretching shift on the alkali ion size and on the Si/Al ratio was observed for various alkali ions exchanged zeolites with various amounts of aluminum atom in the framework. Sanchez-Sanchez and Blasco[3] showed that the shift of the broad peak corresponding to N–H stretching vibration increases from –90 to –230 cm^{-1} in aluminum rich zeolite Y. Intensities and shapes of these peaks depend on the alkali metal ion. Experimental IR spectra obtained for alkali metal exchanged high-silica ZSM-5 zeolite show a similar red shift of N–H stretching vibration (from –100 to –230 cm^{-1}). In this case two distinct peaks are observed the relative size of which depends on the Si/Al ratio and the size of the cation[4].

No information about the structure and coordination of pyrrole on alkali metal ion exchanged zeolite is available from experimental data. In this contribution we present the results of computational study aimed at understanding the details of the structure and character of the interaction of pyrrole with alkali metal exchanged zeolites.

METHODS AND MODELS

Two types of models were used. A cluster model describes the molecule of pyrrole, alkali metal ion (Li$^+$, Na$^+$, and K$^+$), and a part of the zeolite framework surrounding the interacting complex at the *ab initio* level. A hybrid quantum mechanics/interatomic potential function (IPF) approach combines the *ab initio* description of a part of the system with the interatomic potential function description of the remaining atoms (QM-pot model[6]). Within this model the topology of the zeolite framework is respected. The interaction of pyrrole with the extra-framework alkali metal cation was studied for the cation charge-compensating the framework AlO$_4$ tetrahedron with Al atom at T12 position (alkali metal cation in type II position on the channel intersection; see ref.[7] for details). Geometry optimization and calculations of IR spectra of the optimized structures were performed for both model types. Cluster models and quantum mechanical part of the hybrid model were described at the DFT level employing the B3LYP functional[8,9] and a valence triple-ζ-plus-polarization function basis set for O, Li, Na, and K atoms and with a valence double-ζ-plus-polarization function basis set for Al, Si, and H atoms[10,11].

In both approaches (cluster model and QM-pot model) the interaction energies of pyrrole with the M^+/ZSM-5 system were defined as the negative energy of reactions:

$$\text{pyrrole} + M^+/\text{ZSM-5} \rightarrow \text{pyrrole}/M^+/\text{ZSM-5 .}$$
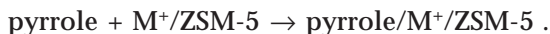
Hence, in addition to the lattice energy minimizations of the pyrrole/M^+/ZSM-5 system the lattice energy minimizations of the M^+/ZSM-5 had to be carried out. At the QM-pot level these geometry optimizations were carried out with the same definition of the inner and outer region as for the corresponding pyrrole/M^+/ZSM-5 system. The calculations of N–H stretching frequency shifts were performed within the harmonic approximation. It should be noted that the use of harmonic approximation for the description of the hydrogen-bonded system is problematic. However, the goal of this study is to investigate the effect of the model on the frequency shift of N–H stretching vibration. We believe that for this purpose the harmonic approximation provides qualitatively correct answers.

Cluster Models

The geometry obtained from QM-pot optimization of the M^+/ZSM-5 system[7] was taken as a initial geometry of the cluster. Geometry optimizations of the pyrrole/M^+/zeolite system were performed with frozen positions of atoms representing the zeolite framework while geometry of pyrrole and M^+ was fully relaxed. The vibrational frequencies were calculated for structures employing the harmonic approximation. Cluster models of various sizes representing the zeolite framework were used. Cluster notation derives from the number of framework T-atoms (Al or Si) in the model (0-T, 3-T, 5-T_d, and 6-T_d cluster models are depicted in Fig. 1). Two types of cluster boundaries were used: (i) all oxygen atoms on the edge of the cluster model are saturated with hydrogen atoms (OH termination) or (ii) all silicon atoms on the cluster edge were saturated with hydrogen atoms (H termination). When the AlO_4 tetrahedron was on the edge of the model (3-T model) it was always OH-terminated. 0-T model, depicted in Fig. 1a, does not contain any atom of the zeolite framework. This model describes a complex of a molecule of pyrrole and a bare alkali metal ion in gas phase. Even if this model is not relevant for the study of interaction inside the zeolite pores, it is still useful to analyze the results obtained with this model and to gain a better understanding of the character of this interaction. 3-T model, depicted on Fig. 1b, consists of three TO_4 tetrahedra (one Al and

two Si framework atoms) interacting with M^+. Both OH-terminated ($AlH_8O_{10}Si_2$) and H-terminated ($AlH_8O_4Si_2$) clusters were used in order to investigate the effect of the cluster boundaries. 5-T_d model, depicted in Fig. 1c, consists of AlO_4 tetrahedron surrounded by four $OSiH_3$ tetrahedra (H-terminated $AlH_{12}O_4Si_4$ cluster). 6-T_d model, depicted in Fig. 1d, is an extension of previous model by additional $OSiH_3$ tetrahedron (H-terminated).

Hybrid Quantum Mechanics/Interatomic Potential Function Model (QM-pot)

In the QM-pot approach the finite inner part describing the site of interest (a complex containing pyrrole molecule, alkali metal ion and surrounding part of the ZSM-5 framework) was treated at the B3LYP level (the same set
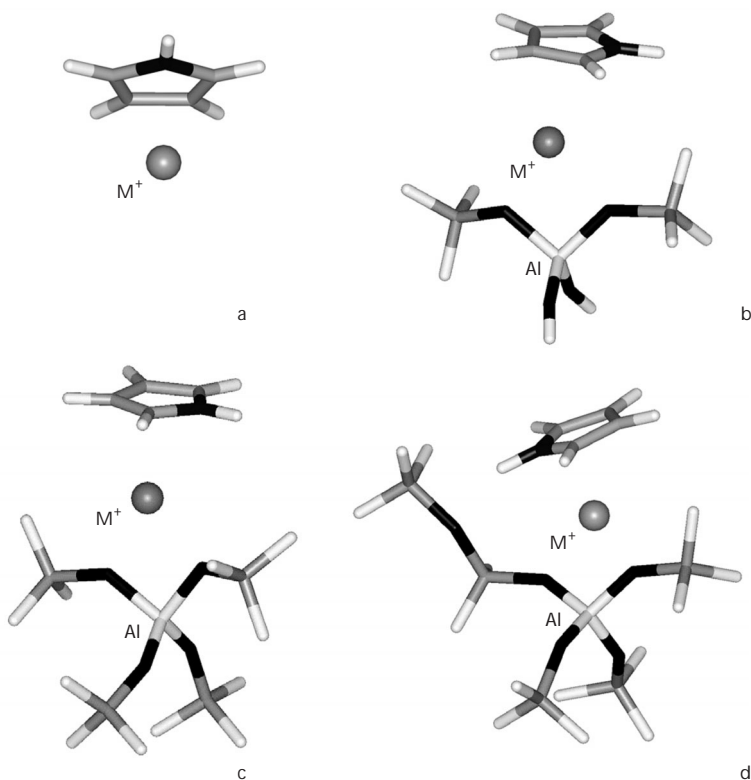

FIG. 1

Definition of the cluster model used in this study: 0-T (a), 3-T (H-terminated) (b), 5-T_d (c), and 6-T_d (d) models. Metal atom is depicted as a circle, framework atoms and pyrrole in the tube mode. Framework Al, Si, and O atoms are in white, grey, and black, respectively. Cluster terminating H atoms are white and the N atom of pyrrole black

of basis function as for the cluster model was used). Inner part of the size of pyrrole/M^+/$AlSi_5O_{19}H_{14}$ was used. Overall six TO_4 tetrahedra form a chain on the edge of the channel intersection (see Fig. 4 for details). Oxygen atoms on the edge of the inner part were saturated with the hydrogen atoms (OH termination). The internal part was embedded in the surrounding periodic zeolite framework (outer part). Interactions outside the inner part (outer part) and the cross interactions between the atoms of the inner and outer parts were treated with the core-shell model ion-pair potential with parameters for Si, Al, O, and H atoms taken from ref.[12], parameters for Na^+ from ref.[13], and parameters for Li^+ and K^+ from ref.[7] Intra-molecular parameters of pyrrole molecule were taken from AMBER package[14]. UFF parameters were used for the description of inter-molecular interaction of pyrrole molecule with zeolite[15]. It should be noted that for the definition of the inner part of QM-pot model used in this study the interaction of pyrrole with surrounding zeolite framework is described at the B3LYP level and the UFF parameters are used only for the description of the pyrrole interaction with distant atoms of zeolite framework. Thus, the error due to the use of relatively unreliable UFF parameters is negligible. The polarizability was taken into account only for O^{2-} anions. Periodic boundary conditions were applied to a unit cell containing 96 T-sites of zeolite framework (95 Si atoms, 1 Al atom), 192 oxygen atoms, 1 atom of the alkali metal, and a pyrrole molecule). The lattice energy minimizations were performed in P1 symmetry. No constraints were imposed in the energy minimization. The vibrational frequencies were calculated for structures at the combined QM-pot level, employing the harmonic approximation.

The calculations were carried out with the QMPOT[16] program, which makes use of the TURBODFT[17] and GULP[18] programs for DFT and shell model potential calculations, respectively. Calculations of vibrational frequencies were made with the GAUSSIAN[19] program suite.

RESULTS

Interaction energies of pyrrole with M^+/zeolite and changes of the N–H stretching frequencies found for particular models are summarized in Table I. Only the values for global minima are reported (for some models several local minima were found in addition).

0-T model: Alkali metal ion interacts with the pyrrole π-system (structure of Li^+/pyrrole is depicted in Fig. 1a). The distances between the alkali metal ion and the plane of pyrrole ring are 1.93, 2.50, and 3.02 Å for Li^+, Na^+, and K^+ ions, respectively. Interaction energy decreases with increasing ion size.

The N–H stretching frequency is lowered by 64, 41, and 32 cm^{-1} for Li$^+$, Na$^+$, and K$^+$ ion, respectively. The red shift is caused by electron withdrawing from the π-system of pyrrole to the alkali ion.

3-T model (H-terminated): Interaction energies of pyrrole with the M$^+$/zeolite system (15, 13, and 12 kcal/mol for Li$^+$, Na$^+$, and K$^+$ ion, respectively) found with this model are significantly smaller than those found with the 0-T model. Natural bond orbital analysis (NBO) shows that the alkali ion withdraws electrons predominantly from the AlO$_4$ tetrahedron and, as a result, the charge on alkali metal ion interacting with pyrrole is less than 1. Interaction energies found with the 3-T model are less than half of those found with the 0-T model for Li$^+$ and Na$^+$ ions; however, interaction energies are reduced only by 25% going from the 3-T to 0-T model for K$^+$ ion. This is due to the fact that the global minimum structure found for Li$^+$ and Na$^+$ ion (depicted in Fig. 1b) is qualitatively different from that found for K$^+$ ion (Fig. 2). In the latter case pyrrole forms a strong hydrogen bond (H-bond) to the Al–O–Si oxygen and K$^+$ ion is pushed towards the edge of the cluster where it interacts with the OH group terminating the AlO$_4$ tetrahedron. Smaller changes of N–H stretching vibration found with the 3-T model for Li$^+$ and Na$^+$ ions (compared with those obtained with the 0-T model) are also due to the fact that the charge transfer from pyrrole to alkali metal ion is reduced. The huge change of the N–H stretching vibration found for K$^+$ is due to the H-bond formation. The weaker interaction of pyr-

TABLE I
Interaction energies of pyrrole with the M$^+$/zeolite model and N–H frequency shifts upon the pyrrole adsorption on the M$^+$/zeolite system calculated with cluster models of various sizes and with QM-pot model

Model[a]	E_{int}, kcal/mol			Δν, cm^{-1}		
	Li$^+$	Na$^+$	K$^+$	Li$^+$	Na$^+$	K$^+$
0-T	39	28	16	–64	–41	–32
3-T (H)	15	13	12	–34	–28	–335
3-T (OH)	14	16	15	–265	–308	–338
5-T$_d$	15	14	10	–25	–27	–22
6-T$_d$	15	14	10	–66	–35	–44
QM-pot[b]	27	22	17	–123	–89	–64

[a] For cluster model definition, see the text and Fig 1. [b] For QM-pot model definition see the text and Fig. 4.

role with Li^+/zeolite and Na^+/zeolite systems found with 3-T model corresponds to the increase in the distance of M^+ from the plane of pyrrole ring (2.36 and 2.62 Å for Li^+ and Na^+, respectively). On the contrary, the distance of M^+ from the plane of pyrrole ring is slightly decreased going from the 0-T to 3-T model (3.02 and 2.95 Å, respectively) for K^+ ion. It should be pointed out that both structure types, with and without H-bond formation (Figs 1b and 2, respectively), were found for all the three alkali metal ions. The structure without H-bond is the global minimum for Li^+ and Na^+ ions and the structure with H-bond is the global minimum for the K^+ ion.

3-T model (OH-terminated): Rather different structures were found with this model compared with the 3-T model (H-terminated): the pyrrole π-system interacts with metal ion and, in addition, pyrrole forms a H-bond to
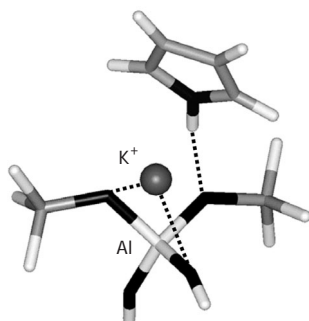

F<small>IG</small>. 2

Interaction of pyrrole with K^+/zeolite modeled with the 3-T (H-terminated) model. The K^+ ion interacts with Al–O–Si and Al–O–H oxygen atoms. For colors, see Fig. 1
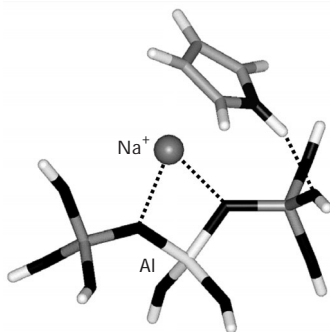

F<small>IG</small>. 3

Interaction of pyrrole with Na^+/zeolite modeled with the 3-T (OH-terminated) cluster model. For colors, see Fig. 1

oxygen atom of cluster termination OH group (see Fig. 3 for details). Interaction energies (14, 16, and 15 kcal/mol for Li$^+$, Na$^+$, and K$^+$ ions, respectively) are slightly larger than those found with the H-terminated 3-T model due to the H-bond formation. A rather large red shift of N–H stretching (–265, –308, and –338 cm^{-1} for Li$^+$, Na$^+$, and K$^+$ ions, respectively) is also due to the H-bond formation with oxygen of the cluster terminating OH group. The oxygen atom of the cluster terminating OH group (Si–O–H sequence) is more basic than framework oxygen atom (Si–O–Si sequence); thus, it forms stronger H-bond associated with larger red shifts.

5-T$_d$ model (H-terminated): The global minimum structure is of the same type for all three alkali metal cations considered (see Fig. 1c for details). The optimized structure is very similar to that found for Li$^+$ and Na$^+$ ions with 3-T H-terminated model. Since no terminating OH group is present in this model (compared with the 3-T H-terminated model where the AlO$_4$ tetrahedron is terminated with two OH groups) the structure found for K$^+$ ion with the 3-T H-terminated model cannot be formed. Interaction energies and N–H stretching shifts reported in Table I are very similar for both the 3-T H-terminated and 5-T$_d$ cluster model (except for K$^+$ ion; see above).

6-T$_d$ model (H-terminated): Interaction energies found with this model are the same as for the 5-T$_d$ model. However, the N–H stretching shifts (–66, –35, and –44 cm^{-1} for Li$^+$, Na$^+$, and K$^+$ ions, respectively) are larger with the 6-T$_d$ model than with the 5-T$_d$ model. The largest difference can be observed for Li$^+$ ion where, in addition to the π-system interaction, a weak H-bond ($r_{H \cdots O}$ = 2.22 Å) is formed between the NH hydrogen and framework oxygen atom (Si–O–Si sequence; see Fig. 1d for details). This H-bond interaction was not found for Na$^+$ and K$^+$ cations due to their ion size. In order to form a H-bond with framework oxygen, even a larger model is required for Na$^+$ and K$^+$ ions.

Embedded model (QM-pot): This model fully respects the zeolite topology and properly accounts for long-range interactions. In addition, no constraints in geometry optimization need to be defined for this model. As a result the interaction of pyrrole with M$^+$/ZSM-5 is significantly enhanced (27, 22, and 17 kcal/mol for Li$^+$, Na$^+$, and K$^+$ ions, respectively) and also the N–H stretching shifts are larger (–123, –89, –64 cm^{-1}, for Li$^+$, Na$^+$, and K$^+$ ions, respectively) than those obtained with small cluster models. The structure of pyrrole interacting with Li$^+$/ZSM-5 (intersection site) is depicted in Fig. 4. For all the ions considered, the H-bond is formed to framework oxygen (Si–O–Si sequence) in addition to the pyrrole π-system interaction with cations. The H-bond is formed between the NH and framework oxy-

gen atom which is rather distant from the AlO_4 tetrahedron to which the alkali metal ion is bonded. As can be seen in Fig. 4, the hydrogen bond is formed to the oxygen atom separated from the AlO_4 tetrahedron by three SiO_4 tetrahedra (Al–O–Si–O–Si–O–Si sequence). The hydrogen bonds are significantly stronger ($r_{H \cdots O}$ = 1.98, 2.09, and 2.07 for Li$^+$, Na$^+$, and K$^+$ ions, respectively) than those found with the 6-T_d cluster model.

DISCUSSION

Based on the experimental data collected for pyrrole adsorbed on high-silica zeolites (ZSM-5) and on aluminum-rich zeolites (Y), it is apparent that two peaks (red shifted by about –100 and –200 cm^{-1} from the pyrrole gas phase value) are due to the N–H stretching vibration[3,4]. Relative population of the peak shifted by –200 cm^{-1} increases with the increasing Al content in the framework. It is assumed that for very high Si/Al ratios, only peak shifted by –100 cm^{-1} occurs. This computational study focused on the description of such high-silica system (ZSM-5 with a Si/Al ratio of 95 in combined QM-pot model). Therefore, below we evaluate the reliability of models used in this study based on the comparison of the calculated N–H stretching frequency shift with an experimental shift of –100 cm^{-1}.
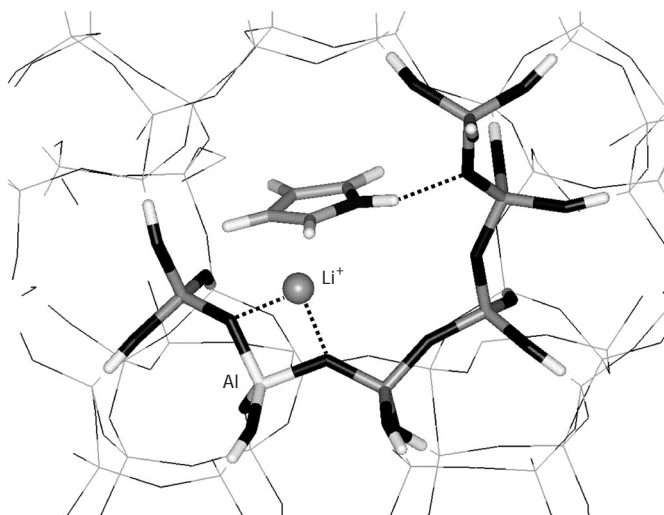

Fig. 4
Interaction of pyrrole with Li$^+$/zeolite modeled with the combined quantum mechanic/interatomic potential function model. Inner and outer part atoms are depicted in the tube and wire modes, respectively. For colors, see Fig. 1

Interaction of bare alkali ion with the π-system of pyrrole causes a red shift of the N–H stretching frequency of –64, –41, and –32 cm^{-1} for Li$^+$, Na$^+$, and K$^+$ ion, respectively. As can be seen from Table I (comparing 0-T and 5-T$_d$ model results), these red shifts become significantly smaller when alkali metal cation is in the vicinity of the AlO$_4$ tetrahedron. However, small red shifts calculated with cluster models employed in this study do not correspond to the experimental results. Another effect must be responsible for a larger red shift of the N–H stretching mode.

The results obtained with the 3-T (OH-terminated) cluster model indicate that formation of the H-bond between hydrogen atom of the NH group and oxygen atom of the cluster terminating OH group is accompanied by a large red shift (ca. 300 cm^{-1}). In this case, however, the H-bond strength is overestimated (larger basicity of O atom of the Si–O–H sequence than that of the Si–O–Si sequence) and calculated red shifts are too large. The only model which predicts the N–H stretching frequency change for high-silica zeolite in agreement with experiment is the hybrid QM-pot model. This model shows that the pyrrole π-system interacts with the metal cation and N–H forms a H-bond with the framework oxygen atom. A stronger H-bond characterized by a shorter H···O distance and a larger N–H stretching frequency red shift can be formed with a framework oxygen atom distant from the AlO$_4$ tetrahedron than with a framework oxygen atom separated from AlO$_4$ tetrahedron by only one Si atom.

Comparing the results obtained with various cluster models it is apparent that the interaction of pyrrole with M$^+$/zeolite is primarily driven by the interaction of pyrrole π-system with the metal cation (10–15 kcal/mol stabilization) and that the system is further stabilized by H-bond formation (1–5 kcal/mol). On the contrary, the N–H stretching red shift is primarily due to the H-bond formation and the interaction of pyrrole with metal cation has only a minor effect on the stretching frequency.

The results presented in this study clearly show that the use of the cluster model for description of the interaction of molecules with active sites in zeolite is at least problematic. Relatively similar cluster models may show qualitatively different results. The OH termination of cluster represents more realistic boundary conditions than the H termination of cluster. In the former case, the framework Si atom on the edge of the cluster is substituted by H atom which has a similar electronegativity, while in the latter case the framework O atom is substituted by H atom. However, our results indicate that the use of the OH-terminated cluster in the study of the interaction with molecules with H-bond formation ability is rather dangerous and may lead to unrealistic description of the situation. Also, based on the

results with small cluster models (3-T cluster in particular), one can errone-ously conclude that the character of the pyrrole interaction with M^+ zeolite is different for small (Li^+ and Na^+) and large (K^+) cations.

Few comments on the reliability of cluster models for description of the pyrrole interaction with M^+/zeolite system: (i) Cluster should not contain any terminal OH groups in order to avoid the formation of very strong but unrealistic H-bonds. (ii) The minimum size cluster model for a proper de-scription of the interaction of the pyrrole π-system with M^+/zeolite is $5\text{-}T_d$ cluster. However, this model does not allow the H-bond formation. (iii) The minimum size cluster model for description of both π-system interaction and H-bond formation is the $8\text{-}T_d$ cluster model formed from the $5\text{-}T_d$ cluster model by threefold SiO_4 expansion in one dimension. (iv) Even if a large cluster model is used, the problems associated with the definition of the starting geometry of atoms representing the zeolite framework and prob-lems with the definition of the geometry constraint imposed in the optimi-zation persist.

Only the combined QM-pot model gives the N–H stretching frequency shift in agreement with experiment. There are several differences between combined QM-pot model and cluster models used in this study: (i) no con-straints in the geometry optimization are employed with the QM-pot model, (ii) OH-terminated inner part of the QM-pot model can be used without a risk of obtaining H-bond with the atoms on the inner part boundary, (iii) interaction of pyrrole with all framework atoms in the peri-odic unit cell is included. As a consequence, inner part of the QM-pot model containing only six TO_4 tetrahedra is a realistic model of the zeolite. On the contrary, at least eight TO_4 tetrahedra are required when the cluster model is used. We conclude that for the study of pyrrole interaction with the M^+/zeolite system, the use of the QM-pot embedding model is more re-liable and computationally less demanding than the use of the cluster model.

CONCLUSIONS

Interaction of pyrrole with alkali metal exchanged zeolite is mainly driven by the interaction of the pyrrole π-system with the alkali metal ion. The in-teraction is further enhanced by the formation of H-bond between NH and the framework oxygen atom (Si–O–Si sequence). This H-bond is the stron-gest when it is formed with the framework oxygen atom separated by two or three SiO_4 tetrahedra from the AlO_4 tetrahedron charge-compensated by alkali metal ion. The interaction of pyrrole π-system with metal cation has

a rather minor effect on the N–H vibrational frequency. The large N–H red shift observed experimentally is due to the H-bond formation.

The use of the cluster model for description of pyrrole interaction with M^+/zeolite site is rather problematic. In order to describe this interaction, the cluster model should consist of at least eight TO_4 tetrahedra and H termination should be used on the cluster boundaries (py/M^+/AlSi$_7$O$_7$H$_{18}$). However, even with this relatively large model, problems with the definition of the initial structure and optimization constraints persist. It is shown that the use of combined quantum mechanics/interatomic potential function model (QM-pot) is advantageous: (i) an inner part of smaller size than eight TO_4 tetrahedra can be used; thus, smaller demands on computer time are required, (ii) geometry optimization without any constraints can be performed, and (iii) more realistic boundaries of inner part (OH terminating) can be used.

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