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Comparative energies of Zn(II) cation localization as a function of the distance between two forming cation position aluminium ions in high-silica zeolites

NELLY A. KACHUROVSKAYA^{1,*}, GEORGII M. ZHIDOMIROV²
and RUTGER A. VAN SANTEN¹

¹ *Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands*

² *Boreskov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk 630090, Russia*

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Abstract—Periodical calculations of Zn(II) metal cation stabilization in cationic positions with distantly placed aluminium ions has been performed for high-silica ferrierite. It was found that decrease of the stabilization energy at large distances between Al ions (more than 10 Å) is about of 2 eV in comparison with nearest possible position of two Al ions in the zeolite lattice and weekly depended on following increase of the Al—Al distance. Main changes in stabilization energy occurred within a 3-Å interval of these distances. Only for the localizations of both Al ions in one zeolite ring zinc cationic form is more stable than hydrogen form.

Keywords: High-silica zeolites; sitting of Zn²⁺; periodic calculations.

INTRODUCTION

The possibility of two-valent metal cation M(II) stabilization in high-silica zeolites at the isolated aluminium occupied oxygen tetrahedra distantly placed from each other was shown by Kazansky and co-workers for a number of two valence metals including Zn [1–3]. It was found by DRIFT study of dihydrogen adsorption anomal large stretching frequency shift in adsorbed H₂ molecule and dissociation of dihydrogen at elevated temperature. The comparison of the data for zeolites with increasing zeolite module (Si/Al ratio) allowed to associate this behavior with the dihydrogen adsorption on M(II) in above mentioned unordinary form of cationic positions in zeolites. Theoretical treatment of the molecular and dissociative adsorption of H₂ on Zn(II) in such type cationic position [4] was in good agreement

*To whom correspondence should be addressed. E-mail: N.A.Kachurovskaya@tue.nl

with the experiment. It is evident that stabilization energy of Zn(II) will decrease with increasing distance between two Al ions, which define the cationic position for the metal cation. We have used VASP periodical calculation of ferrierite with subsequently increasing distance between two isomorphously substituted Al ions in the zeolite lattice in order to study this dependence. We believe that here the periodical approach is much more preferable than finite cluster approximation because of the necessity to provide rather accurate evaluation of the electrostatic interactions in the structures with distantly placed charges.

COMPUTATIONAL DETAILS

Periodic *ab initio* calculations have been performed by using the Vienna Ab Initio Simulation Package (VASP) [5–8]. This code carries out a periodic density functional calculations (DFT) using pseudopotential and a plane-wave basis set. DFT was parametrized in the local-density approximation (LDA), with the exchange-correlation functional proposed by Perdew and Zunger [9] and corrected for non-locality in the generalized gradient approximations (GGA) using Perdew–Wang 91 functional [10].

The interaction between the core and electrons is described using the ultrasoft pseudopotentials (US-PP) introduced by Vanderbilt [11] and provided by Kresse and Hafner [12]. These pseudopotentials allow a drastic reduction of the necessary number of the plane waves per atom. Cutoff 325.0 eV has been used for our calculations. Parameters such as k-point were kept fixed and equal to 1 (Γ -point version of VASP).

The original model consists of one unit cell of ferrierite (orthorhombic cell, $a = 19.156$, $b = 14.127$, $c = 7.489$). It contains 36 TO_2 units per unit cell. Geometry optimization was performed at a constant volume using a quasi-Newton algorithm based on the minimization of analytical forces. When forces on the unit cell atoms were less than 0.05 eV/\AA convergence was achieved.

On the calculations of Zn form electrostatic interaction between defects in neighboring supercells could appear. However, in the case considered it should be small (in the order of 0.1 eV). There are few reasons for this. Zn^{2+} is not in a high-charged state like $3+$, $4+$, ferrierite unit cell possess large lattice constants and finally, charged defects is embedded in a dielectric medium (bulk) and all spurious interactions between neighboring cells are scaled down by the bulk dielectric constant ϵ , which is why dipole correction was not computed.

RESULTS AND DISCUSSION

Two aluminum atoms were placed into the ferrierite framework, substituting two silicon atoms within the same unit cell in framework positions. This substitution corresponds high silica zeolites with Si/Al ratio equals 17. First, the hydrogen form

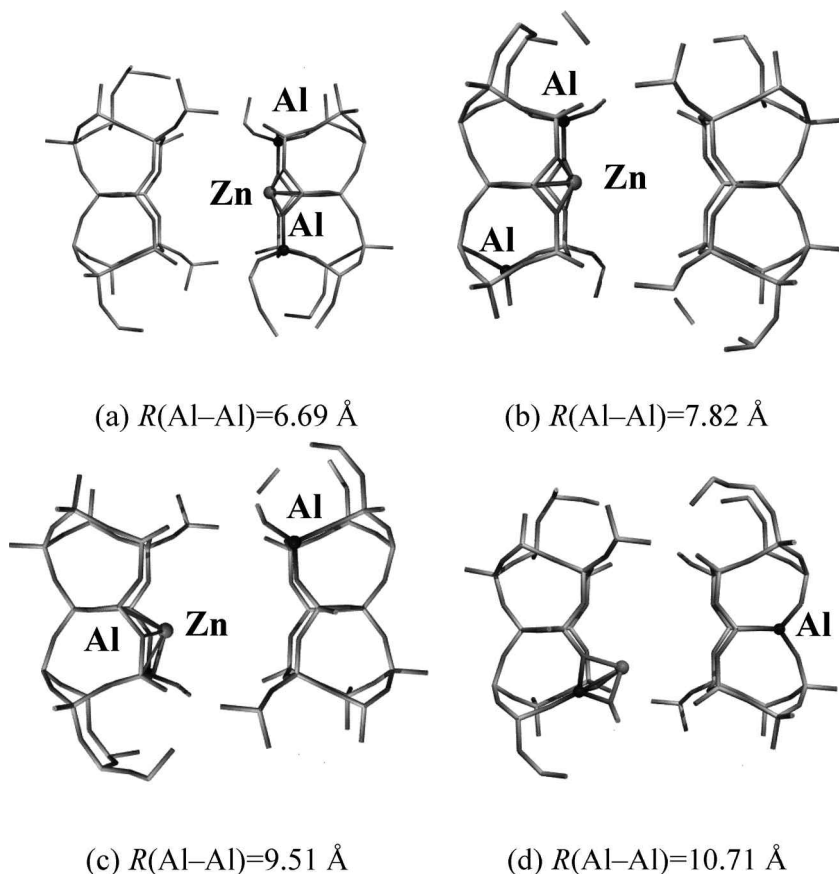
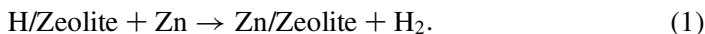


Figure 1. Optimized geometries of the Zn-structures with distant aluminum atoms.

of ferrierite was calculated. Two protons were placed in the nearest to aluminum bridge positions. Substitution on Zn form was considered according to the equation



Four structures with distant aluminum atoms were considered. Their optimized geometries are presented in Fig. 1. The distance between Al atoms were varied from 6.69 Å, when both Al ions are localized in the 6-member zeolite ring, to 10.71 Å, when distance between aluminums in the unit cell is larger compared with the distance to the Al atom in the neighboring unit cell (9.62 Å). In the optimized geometries (Fig. 1a and 1b) Zn^{2+} cations are 4-coordinated and form slightly pyramidal structures. In the structures in Fig. 1c and 1d, Zn^{2+} cations form tetrahedral structures with three oxygen atoms. A graphic representation of the dependence of the unit cell energy on the Al—Al distance for Zn form of ferrierite is shown in Fig. 2. Very fast decreasing of Zn^{2+} stabilization energy was observed with increasing Al—Al distance. It equals about 2 eV in a 3-Å interval. Following increase of the Al—Al distance demonstrates no changes in the stabilization energy.

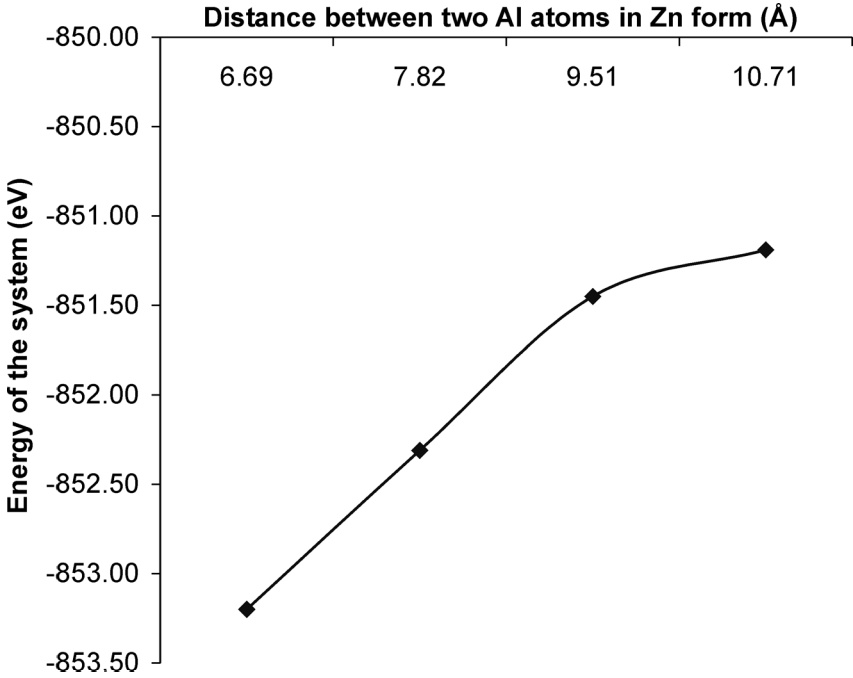


Figure 2. Graphic dependence of the unit cell energy from Al—Al distance for Zn form of ferrierite.

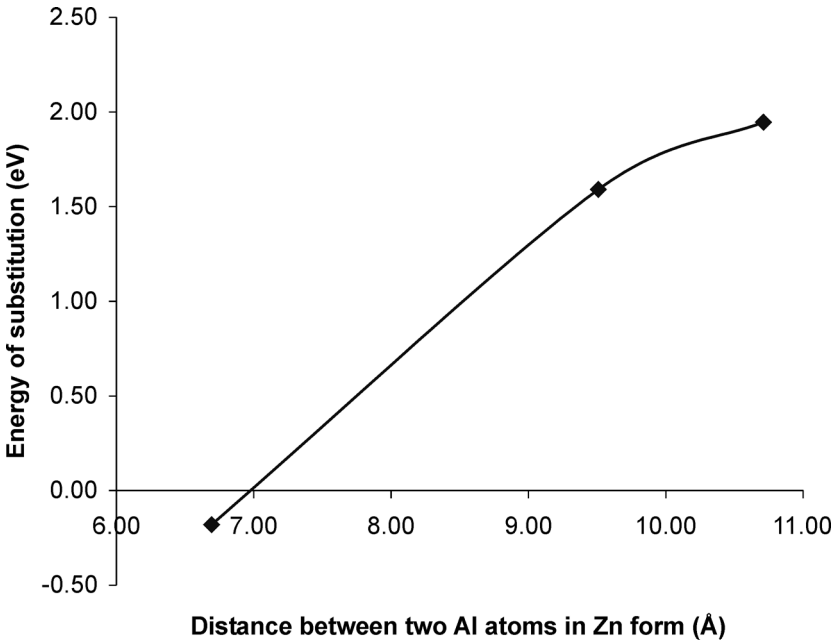


Figure 3. Changes in the energy of the hydrogen substitution on Zn form from Al—Al distances.

Changes in the energy of reaction hydrogen substitution on Zn form from Al—Al distances are shown in Fig. 3. If we consider the energy of the substitution (1) only for the localization of both Al ions in the 6-member ring, the Zn cationic form is more stable than hydrogen one (see Fig. 1a). The energy of substitution equals -4.5 kcal/mol. These data are in qualitative agreement with spectroscopic observations on the preferences siting for the individual cationic sites α , β and γ of divalent ions [13, 14]. Structure 1a is exactly in the α -cationic exchange position. It is interesting to note that DFT cluster model studies predicted some larger Zn^{2+} stabilization energy for α -cationic position [14], probably associated with the difference in the quantum chemical bases of these two calculation schemes.

Finally it should be noted that, although two-valent metal cation prefer the cation position with close positions of Al ions, it does not exclude the possibility of another variants of their stabilization in high-silica zeolites as it was considered above. Metal cations in such unusual cationic positions should be more chemically active and could be identified by a probe molecule spectroscopic study.

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