Quantum-chemical investigation of the formation of Lewis acid centers of high-siliceous zeolites

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Abstract

AM1 quantum-chemical model calcualtions of the dealumination process in high-siliceous zeolites have confirmed the thermodynamical possibility of Lewis center formation mechanism previously suggested by other authors. The structure and local charge distribution for the Lewis centers of two arts produced at this process were studied in detail. The calculated values of the NH_3 and CO adsorption energies on these L-centers allowed for conclusion about their relative acidity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Experimental and theoretical investigations of the catalytic activity of zeolites are of great interest for the contemporary theory of catalysis. A large number of publications in this area was concentrated on the study of zeolites with high contents of the Al atoms. The high-siliceous zeolites with Si/Al ratio more than 10 have been studied to a lesser degree. From the theoretical viewpoint, the main attention was paid to the study of catalytic activity of Brönsted acid centers, whereas the formation and activity of Lewis acid centers (L-centers) have been studied insufficiently [1]. For this reason, the main goal of the present communication was to study quantum-chemically the peculiarity and strength of Lewis centers formed during the treatment of zeolites by water vapor in accordance with the scheme suggested in Ref. [2].

2. Calculational

As a base object we have chosen a zeolite fragment containing 1 Al and 27 Si atoms (Fig.1). The broken boundary bonds of this finite cluster were saturated with hydrogen atoms and its structure was completely optimized using semi-empirical quantum-chemical AM1 method [3] by means of Gaussian 94 program package [4]. This optimized structure

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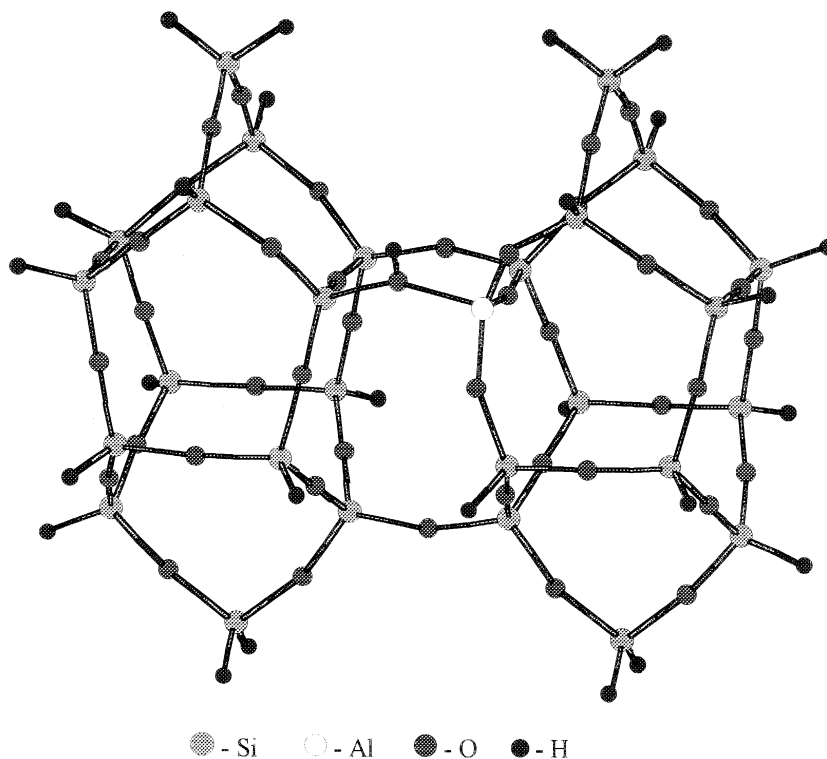
Fig. 1. The zeolite fragment used for quantum-chemical calculations.

was used for all model calculations presented below.

3. Results and discussion

According to Ref. [2], the strength of L-centers in zeolites is caused by electron acceptor properties of the aluminum atoms of lattice defects that are formed in the process of dealu-mination. The authors have suggested consider-ing the dealumination as a three-stage process, with each stage being a dissociative adsorption of one water molecule. These three stages of dealumination with the atomic charge distribu-tion we calculated quantum-chemically (the charges on the hydrogen atoms are omitted) are presented schematically below. For simplicity, only essential structural changes occurring in the dealumination process are shown on these schemas.
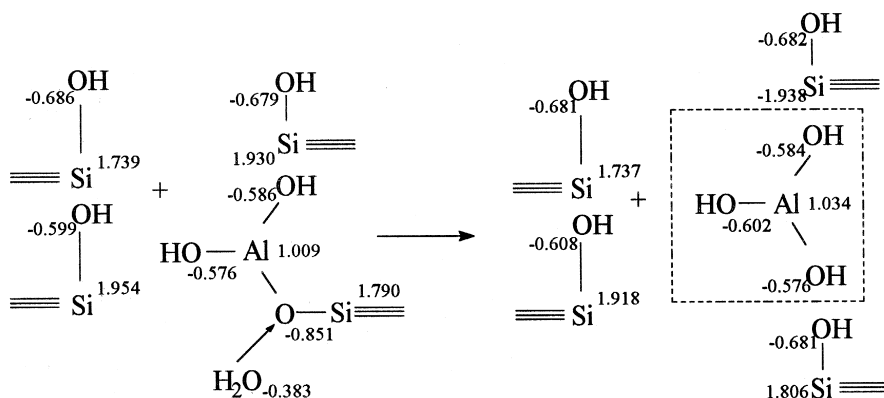
The 1-st stage of dealumination
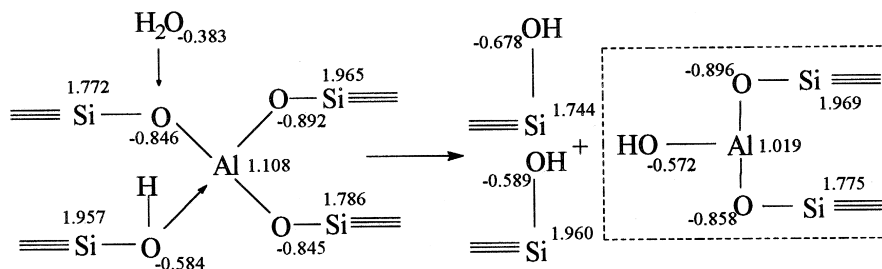
The 2-nd stage of dealumination
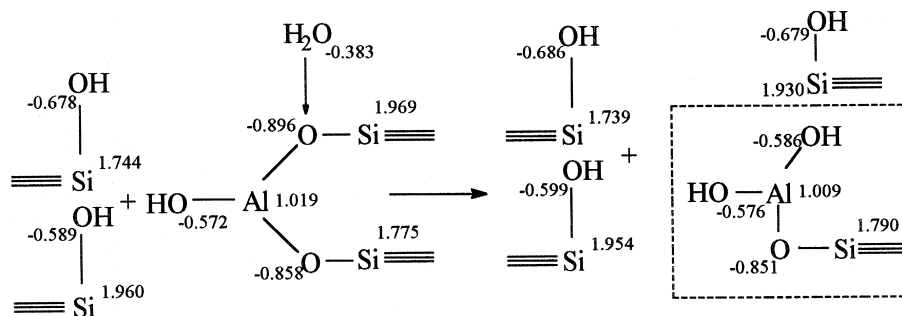
The 3-rd stage of dealumination

The calculated energetical gains for the three stages depicted above are ca. -70, -25 and -15 kJ/mol, correspondingly. Ignoring the entropy corrections ($\Delta G \approx \Delta H$), one can conclude the thermodynamical possibility of these stages of dealumination. The energetical gain between the initial and final structures (ca. -110 kJ/mol) shows the possibility of extraction of $Al(OH)_3$ fragment from the bulk of the crystal lattice. According to Ref. [2], this final product of dealumination can interact with the intermediate structures of single stages of this process and produce L-centers of two arts (see below).

Formation of the L_1-center
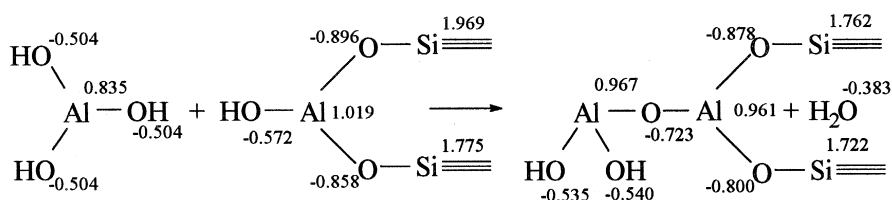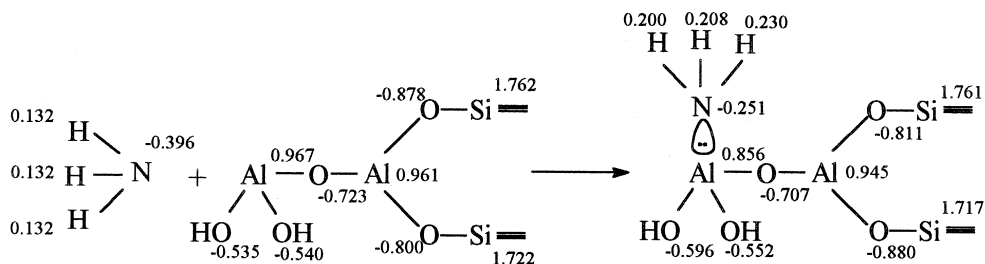
Formation of the L_2-center
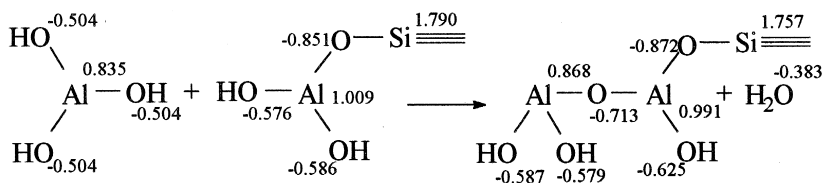
The quantum-chemically obtained energetical gains of L_1- and L_2-centers formation are ca. -38 and -102 kJ/mol, respectively. These results allow the conclusion about the possibility of existence of both L-centers.

As the next step, we have estimated the adsorption energies of NH_3 and CO molecules chosen as probes on the catalytic activity of the L-centers depicted above. For NH_3 molecule, the adsorption energies on the L_1- and L_2-centers are 75 and 23 kJ/mol, whereas CO molecule adsorbs on these centers remarkably weaker (28 and 5 kJ/mol, respectively). The total charges on the adsorbed NH_3 molecule are $+0.387$ and $+0.401$ for the L_1- and L_2-centers, respectively. These data demonstrate the electron charge transfer from the NH_3 molecule to the Al atom. Note that the absolute values of charge transfer are in opposite sequence to the adsorption energy on both centers. In the case of CO adsorption, the total charge on CO molecule is negative. In other words, the electron charge transfer from the L-centers to the adsorbed molecule takes place. This can be explained by the fact that CO molecule is not only a σ-donor but also a π-acceptor and the

acceptor property of CO predominates in the case under consideration. For this reason, NH_3 molecule is probably more appropriate as a probe on the strength of acid L-centers in comparison with CO molecule.

It should be noted that the local geometries of both Al atoms on which the adsorption of NH_3 and CO was considered have practically planar structures and does not differ substantially (Fig.2). The possible reason for the remarkably weaker acidity of the L_2-center compared with L_1-center is probably the less positive effective charge on Al atom of this center due to a negative charge transfer from OH-group (marked by asterisk) having stronger σ-donor properties than the ($-O-Si\equiv$) fragments.

The computed value of the NH_3 adsorption energy on L_1-center is in agreement with the highest possible experimental value estimated in Ref. [5] for three-coordinated aluminum atoms (not higher than 160 kJ/mol). As for CO molecule, its adsorption energy we computed for the same center (28 kJ/mol) is close to the estimations for weak acidity L-centers made in Ref. [6] (34–40 kJ/mol).

NH_3 adsorption on the L_1-center

NH$_3$ adsorption on the L$_2$-center
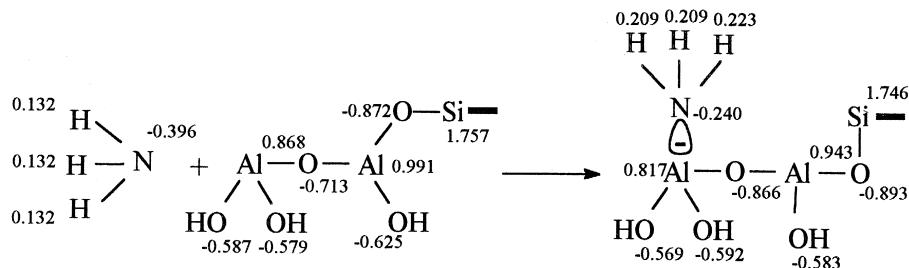
CO adsorption on the L$_1$-center
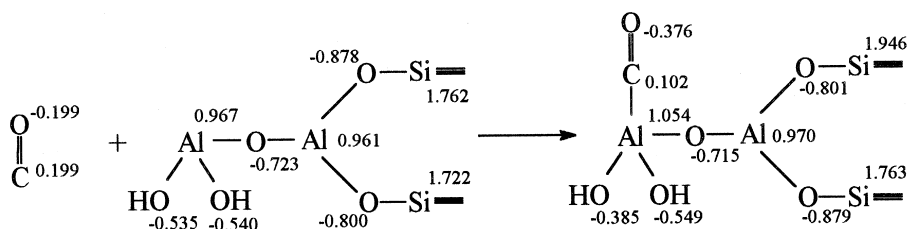
CO adsorption on the L$_2$-center
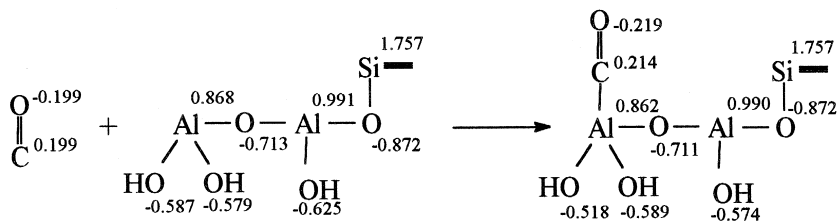
4. Conclusions

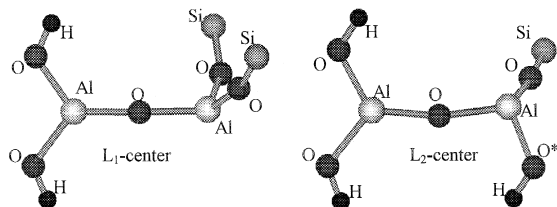The performed quantum-chemical calculations have confirmed the thermodynamical possibility of the dealumination process and Lewis center formation mechanism suggested in Ref. [2]. The acid activity of the L$_1$-center is remarkably higher in comparison with the L$_2$-center. The obtained results do not exclude the existence of other L-centers with stronger acidity.

Fig. 2. Local geometrical structures of L-centers

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