QUANTUM CHEMICAL STUDY OF THE INFLUENCE OF THE ZEOLITE ELECTROSTATIC FIELD ON THE PHYSICAL CHARACTERISTICS OF ETHYLENE

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A modified CNDO/2 method whose Hamiltonian includes the terms describing the interaction of electrons with the electrostatic field of the zeolite crystal is employed for studying the influence of the faujasite electrostatic field on the physical characteristics of ethylene. It is shown that this field causes significant changes in the distribution of electron density in the ethylene molecule as a function of its orientation and localization in the large cavity of faujasites.

Zeolitic catalysts are known to find their primary application in various transformations of hydrocarbons [1-2]. Consequently, the knowledge of the ways in which the zeolite catalyst acts on hydrocarbons is necessary for a better understanding of such processes. While the acidic centers of zeolites (Brönsted or Lewis) were proved to play an active role in hydrocarbon reactions on zeolites, the role of the electrostatic field operating in the zeolite pores remains a subject to be discussed [1-3]. For that reason, this work is devoted to a quantum chemical study of the influence of the zeolite electrostatic field on the physical characteristics of ethylene situated in the large cavity of faujasites.

In the calculations, a modified version [4-5] of the CNDO/2 method was employed. Its Hamiltonian includes terms describing the interaction of electrons (or core charges) of the molecule with the point charges located in the positions of the zeolite crystal atoms and bearing the corresponding charges calculated [6] for individual types of the atoms. The CNDO/2 method is known to overestimate energy values. This, however, does not prevent us to use this method for qualitative estimation of energy changes caused by polarization of a molecule. The zeolitic skeleton was here modelled [4, 5] by ten cubo-octahedra in the form of 720 point charges; i.e. by 240 point charges $Z_T = 1.5$, representing...
Si or Al atoms, and by 480 point charges \( Z_0(Z_0 = -Z_T/2) \), corresponding to O atoms. The position of these point charges were taken from X-ray data [7], the geometry of ethylene (\( d_{C-C} = 1.37 \times 10^{-10} \) m, \( d_{C-H} = 1.07 \times 10^{-10} \) m, HCH angle = 120°) from Ref. [8]. Two types of the localization of ethylene in the large cavity of faujasite (formed by ten mentioned cubo-octahedra) were considered (cf. Fig. 1): A) the C=C bond was situated on the \( C_{3v} \) axis of the zeolite; B) the center of the C=C bond was on the \( C_{3v} \) axis which lay in the ethylene plane, the C=C bond being perpendicular to the \( C_{3v} \) axis; in both of these cases the ethylene plane was situated in the plane given by the \( C_{3v} \) axis and the T atom forming the six-fold zeolitic window perpendicular to the \( C_{3v} \) axis. The distances between the \( S_{II} \) cationic position of the zeolite and the C=C bond center were 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 \( \times 10^{-10} \) m, resp.

The effect of the zeolite electrostatic field on the total CNDO/2 energy and the dipole moment of the ethylene molecule, as a function of its position and orientation, is depicted in Fig. 1. The ethylene molecule is polarized by the electrostatic field and its total CNDO/2 energy is decreased in comparison with the energy of the isolated molecule. This is particularly valid if the molecule is situated close to the \( S_{II} \) cationic position, while with the increasing distance between the \( S_{II} \) position and the ethylene molecule these effects become less.

Fig. 1. Depiction of changes in the total CNDO/2 energy (full lines) and dipole moment (dotted lines) of the ethylene molecule as a function of the distance of its center from the \( S_{II} \) cationic position for orientations A and B.