597d Calibration of an Electronegativity Equalization Method Based on Dft Results to Evaluate the Partial Charges, Global Softness, and Local Softness of Zeolite Structures

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Prediction of catalytic activity can be achieved through the knowledge of chemical descriptors such as partial charges, Fukui functions and global softness. These descriptors are accessible through ab-initio DFT calculations. However, the size of certain catalytic materials such as zeolites makes the use of DFT calculations very computationally expensive. Currently, DFT studies of zeolites are done on embedded clusters that represent the active site and the environment around it. However, if the effects of local and distant changes in composition and structure on the partial charge and softness of individual atoms wants to be studied for a large number of structures and compositions, the DFT methods are still prohibitive. The Electronegativity Equalization Method (EEM)[1] is a robust, fast semi-empirical method that enables the calculation of partial charges, Fukui functions and global softness for molecules and crystalline solids at a fraction of the cost of DFT calculations. When applied to solids, the electrostatic contribution to the electronegativity equalization must be generated by an Ewald sum [2]. It has been shown that after proper calibration of χ * (electronegativity) and η *(absolute hardness) for each constituent atomic type, the EEM-calculated partial charges for organic molecules not included in the calibration set agree very well with ab-initio partial charges of the same molecules [1,3]. This work deals with the development and calibration of a program that implements the EEM to zeolites of different structure and composition. This program is able to correctly choose the Ewald sum parameters to ensure proper and fast convergence. Previous calibrations [4] of χ * and η * for Al, Si, O and H were based on small molecules containing such atoms. In contrast, our calibration was based on structures that include H-ZSM-5, H-chabazite, H-mordenite and H-faujasite. Mulliken partial charges where obtained from embedded cluster calculations at the DFT level. A distinct feature of the this study is that the bond lengths and bond angles used to calculate the interatomic distances required by the EEM equations were taken from the Al-free zeolite structures regardless of the actual Si/Al ratio. Thus, the effects of lattice relaxation were completely absorbed into the parameters of χ * and η *. When the χ * and η * parameters were applied to zeolite structures not contained in the calibration set, the EEM partial charges successfully reproduced the corresponding DFT Mulliken partial charges.

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