

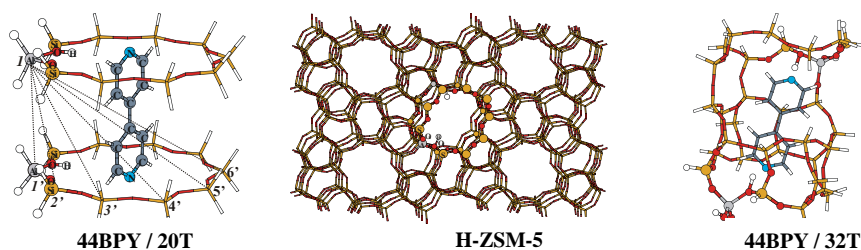
Theoretical Study of the Dispersive Interactions Effects on the Adsorption properties of 4,4'-Bipyridine in H-ZSM-5 Zeolite

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The effects of the zeolite framework on the adsorption of bidentate 4,4'-bipyridine (44BPY) ligand in the straight channel of H-ZSM-5 (Z) has been investigated by DFT calculations using M06-2X functional to account for dispersive interactions [1]. The straight channel is simulated by two clusters constituted of 20 and 32 tetrahedra (T). These clusters have two Al atoms located at positions sufficiently distant from each other allowing the bidentate 44BPY to interact with the two Brønsted acid sites of the zeolite.



The minimum energy pathways of the double proton transfer from H-ZSM-5 to 44BPY ligand were calculated. The potential energy surfaces are characterized by two minima corresponding to the monodentate $44BPYH^+/Z^-$ and bidentate $44BPYH_2^{2+}/Z^{2-}$ ion pair complexes. No energy minimum is found for neutral hydrogen bonding structure.

Two monodentate ion pair complexes differing by the protonated pyridyl ring may be formed, which leads then to the formation of the bidentate $44BPYH_2^{2+}/32T^{2-}$ complex via two distinct pathways. The relative stability between all adsorption complexes involved in this double proton transfer does not exceed 5 kcal mol^{-1} .

Our results clearly show that the adsorption energy of 44BPY is mainly due to the effects of the zeolite framework executed through dispersive van der Waals interactions. These interactions decrease the relative stability of mono and bidentate complexes and stabilize the transition state connecting them. Consequently, an equilibrium between the two mono- and bidentate minima can be established on a flat potential energy surface.

The calculated vibrational frequencies and frequency shifts of 44BPY adsorbed as mono- or diprotonated species are in good agreement with available experimental data.

[1] Y. Akacem, M. Castellà-Ventura and E. Kassab, J. Phys. Chem.A 116 1261-1271 (2012).