DFT Study of the Steric Effect on Some Methyl Pyridines Adsorption in Zeolite

MARTINE CASTELLA-VENTURA[1] AND EMILE KASSAB[1]

[1]*Laboratoire de Chimie Théorique, UMR 7616 CNRS, Sorbonne Université, Paris, France*

martine.ventura@lct.jussieu.fr; ek@lct.jussieu.fr

The theoretical study of the adsorption of pyridine (PY) and of its methyl derivatives (isomers of methyl and dimethyl pyridines) on the Brønsted acid sites (BAS) of H-ZMS-5 zeolite cavity by cluster and periodic models, using PBE-D3 calculation method has been investigated. In this study, realistic cluster models extracted from the siliceous crystallographic ZSM-5 structure have been used. The substitution of one Si atom in different tetrahedral crystallographic T-sites by aluminum atom within the ZSM-5 cavity has been considered. The confinement effects resulting from van der Waals dispersion interactions and steric constraints on the energetic and vibrational properties of the adsorption complexes formed have been thoroughly examined.

Our DFT-D3 calculation results clearly show that upon adsorption of any PY derivative, a proton transfer occurs spontaneously from BAS to adsorbed molecule leading directly to the formation of an ion pair complex. Whatever the adsorption complex considered, the calculated structure reflects a compromise between the repulsive interactions due to steric hindrance and the attractive van der Waals dispersion interactions between the atoms of the adsorbed molecule and those of the wall zeolite cluster. Although the isomers of methyl pyridine derivatives have the same stability and the same proton affinity, the stability of their complexes and the adsorption energy of their isomers essentially depend on their steric hindrance due to the fact that for some sites of adsorption, the methyl group of some isomers does not fit well in the void space of the zeolite cavity. Whatever the adsorbed molecule considered, the calculated vibrational frequencies and frequency shifts are in satisfactory agreement with the experimental results available in the literature.

References

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