A DFT-D2 study of BTEX adsorption on rutile TiO_2 (110) surface

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Keywords: BTEX, DFT-D2, Adsorption, TiO_2 rutile

INTRODUCTION

Air pollution is a critical environmental problem in the world, affecting directly the health quality. A typical cause of indoor air pollution is the known volatile organic compounds (VOCs). The major VOCs are the monoaromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (o-xylene, m-xylene and p-xylene)[1]. Altogether, these compounds are known under the acronym BTEX. Rutile TiO_2 is the most abundant polymorphic form, among the natural low index faces the (110) is the most stable. TiO_2 applied to VOCs degradation is a promising technology for the control of these compounds, largely for the BTEX degradation. In this work, we have performed theoretical studies of BTEX adsorption over TiO_2 (110) of rutile.

METHODS

All calculations were performed using DFT with plane wave as basis sets in VASP. Generalized Gradient Appoximation (GGA) was used with the exchange and correlation functional Perdew-Burke-Ernzerhof (PBE) with and without the semi-empirical correction proposed by Grimme (PBE-D2). Adsorption of BTEX molecules were studied using supercells of (3x2) of rutile TiO_2. Atomic positions for BTEX molecules were fully optimized, while for the TiO_2 surface only the atomic positions of half of the layers were relaxed. For the optimization the Quasi-Newton algorithm was used. The energy cutoff was 400 eV, using a k-point grid in the first Brillouin zone of 3×3×1.

RESULTS AND DISCUSSION

The most stable configurations found were the BTEX molecules parallel and perpendicular to the surface with the ring center in a bridge conformation, between bicoordinated oxygen atoms (O_{2C}) and pentacoordinated titanium atoms (Ti_{5C}). This is the BTEX∥TiO_2-rutile and BTEX⊥TiO_2-rutile conformation for the (110) do TiO_2 surface. Fig. 1 shows the optimized system for the benzene∥TiO_2-rutile and benzene⊥TiO_2-rutile using PBE functional.

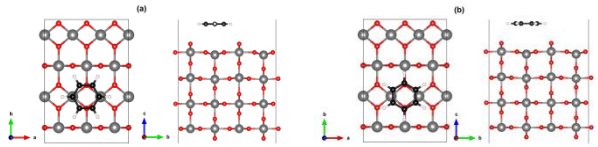

Figure 1. . Optimized (a) benzene∥TiO_2-rutile and (b) benzene⊥TiO_2-rutile.

The adsorption energy of BTEX molecules in the rutile TiO_2 surfaces are shown in Table 1.

Table 1. Adsorption energy of BTEX on TiO_2.

$E_{adsorption}$ (kJ/mol)	BTEX∥TiO_2-rutilo		BTEX⊥TiO_2-rutilo	
	PBE	PBE-D2	PBE	PBE-D2
Benzene	25.00	60.04	25.58	60.18
Ethylbenzene	23.83	72.38	21.86	67.28
Toluene	23.59	65.21	22.65	67.45
o-Xylene	18.72	75.19	16.52	67.99
m-Xylene	19.00	77.98	20.68	71.03
p-Xylene	17.19	93.49	17.58	72.62

CONCLUSIONS

The interaction energies using functional with dispersion correction (PBE-D2) show that the calculations using the PBE functional failure in the description of this interaction, underestimating the adsorption energies.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the FAPEG, CAPES, CNPq, PIQS/IFG, CENAPAD-SP and FAPDF.

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