# Theoretical study of $CO_2$ molecule adsorption on $ZrO_2$ surfaces.

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## Introdução

$ZrO_2$ (zirconia) is a technologically important material used in catalysis, gas sensor and batteries [1]. Zirconia is an active component in the methanol synthesis from the mixture $CO_2/H_2$ [1-3]. Therefore, the zirconia surface properties have been studied using theoretical methods [2].

In this work, we describe the geometry of $CO_2$ interaction with the $ZrO_2$ surface. The structure of tetragonal zirconia was optimized using the density functional PBE1PBE with the program Crystal06. The adsorption of $CO_2$ was studied with the Gaussian03 program also with PBE1PBE functional and 3-21G basis function, through the use of a twelve units cluster of the optimized structure for the (001) surface.

## Resultados e Discussão

Table 1 shows the cell parameters values optimized for zirconia tetragonal phase. The data are comparable to the literature [3]. Figure 1 shows the result of optimized $CO_2$ interaction on the $ZrO_2$ cluster. The monodentate adsorption is found in the carbonates formation, on oxides surfaces, with high basicity [4]. Bands in 1450 and 1425 $cm^{-1}$ are related to this monodentate form [4]. The interaction energy found with the model cluster of -461kJ/mol (with BSSE) is higher than the experimental data [4]. The interaction was studied at very low coverage, thus this difference may be related to interaction absence between $CO_2$ molecules.

The $CO_2$ interaction distance was 2.22Å. The HOMO-3 orbital (Figure 1) presents the $CO_2$ molecule contribution. The interaction with the surface was very strong, which may have led to a change in the $CO_2$ orbital distribution. The optimization of tetragonal $ZrO_2$ cell parameters are in agreement with literature data, showing a good correlation of PBE1PBE hybrid functional. The interaction energy was greater than the experimental data. However, the geometry is correlated to the experimental data. The adsorption of $CO_2$ molecule has a distortion of bond angle, this is due to the interaction of carbonate like specie formation.

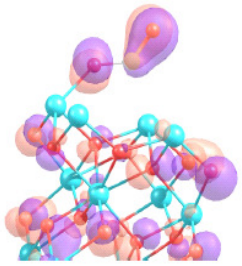

**Figure 1.** $CO_2$ interaction on the $ZrO_2$ surface. Hydrogen atoms for dangling bonding are omitted.

**Table 1.** Cell parameters of tetragonal zirconia (Å).

| | a | c |
|---|---|---|
| PBE1PBE | 3.61 | 5.21 |
| Exp.(a) | 3.64 | 5.27 |
| PW91 [3] | 3.67 | 5.25 |

## Conclusões

The cell parameters of $ZrO_2$ structure are in accordance to the literature. A carbonate like geometry was found for the optimized $CO_2$ adsorption.

## Agradecimentos

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