FT-IR Characterization of Titanium Tetrabutoxide Catalyst of Ethylene Dimerization: A DFT Study

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Abstract

DFT calculations were done to study optimized structure and theoretical FT-IR spectroscopic data for the titanium tetrabutoxide as a conventional catalyst in the ethylene dimerizaiton. The results revealed a tetrahedral structure in gas phase with basic factors of r(Ti...O)=1.81Å and ∠(O–Ti...O)≈108.39˚. Comparison of theoretical and experimental frequencies of vibrational assignments in the FT-IR spectrum showed that all frequencies computed by the DFT had good agreement with those observed in the experimental results.

Background

Ethylene dimerization has triggered much research and scientific effort to improve performance of the catalysts used in the industrial scale. Of the metals studied, titanium-based compounds have been found to be suited, giving high yields of 1-butene. Computational chemistry, and in particular density functional theory (DFT), has been proven to give insights for a better understanding of reaction mechanisms. Vibrational spectroscopy is an excellent method for structural analysis and the determination of molecular interactions.

Methods

GAMESS program package was used to carry out all DFT calculations. B3LYP functional in conjugation with LANL2DZ (Los Alamos National Laboratory second double-zeta) basis set for Ti atom was used to perform geometry optimization and frequency calculations. To achieve reasonable frequency matching, calculated vibrational frequency were multiplied by a scaling factor, 0.964, as determined from data in benchmark Data Base.

Results

Firstly with considering the aforementioned basis set for Ti atom, B3LYP/6-31G basis set was used for C, H, and O atoms.

Results (cont.)

After optimization, configuration of titanium tetra butoxide structure was disrupted (see Fig. 1 (a')). So, optimization method is qualified by the B3LYP/6-31+G (d,p) basis set for all atoms. The optimized structure in gas phase is shown in Fig 1(a").

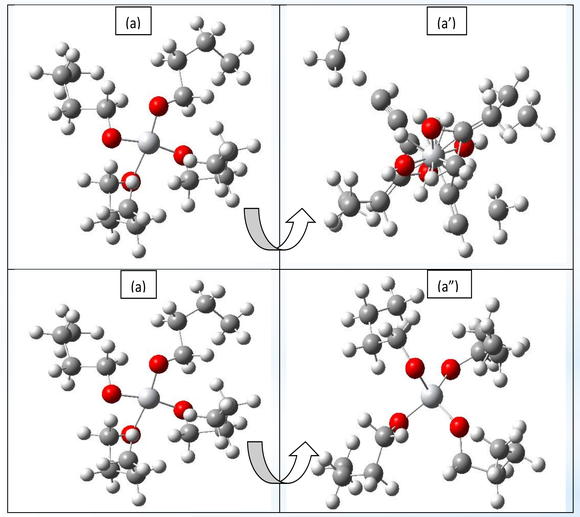

Table 1. The scaled theoretical harmonic wavenumbers (cm^{-1}) of titanium tetra butoxide calculated by DFT.

No	Calculated frequency (cm^{-1})	Vibrational assignments
1	2994.8	ν (C—H) for CH_3 asymetric stretching
2	2988.0	ν (C—H) for CH_2 asymetric stretching
3	2943.4	ν (C—H) for O—CH_2 asymetric stretching
4	2930.1	ν (C—H) for CH_3 symetric stretching
5	2911.3	ν (C—H) for CH_2 symetric stretching
6	2901.8	ν (C—H) for O—CH_2 symetric stretching
7	1463.2	δ(C—H)[a] for CH_2
8	1380.8	δ(C—H)[b] for CH_2
9	1269.2	δ(C—H)[a] for CH_3
10	1167.3	δ(C—H)[c] for CH_2
11	1063.2	ν (C—C—C) asymetric stretching
12	1014.6	ν (C—O) symetric stretching
13	955.5	ρ_r (CH_2)[d]
14	840.7	ν (C—C—C) symetric stretching
15	698.3	ν (Ti—O) stretching

[a] Scissoring (in-plane)vibration. [b] Wagging (out-of-plane)vibration. [c] Twisting (in-plane) vibration. [d] Rocking (out-of-plane)vibration.

The theoretical assignment of the frequencies for titanium tetra butoxide were reported in Table 1. It belongs to C1 group symmetry with 57 atoms and has 19 fundamental modes of vibration.

Conclusion

The principal bonds were portrayed with aid of the DFT calculations. The experimental and theoretical results had a good agreement with each other.

References

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