Catalytic hydrogenation of acrylic acid by molybdenum carbide

Ricardo R. Oliveira[a](PG), Victor Teixeira da Silva[b], Leandro Sousa[b], Alexandre B. Rocha[a](PQ)
[a]*Chemistry Institute, UFRJ, Rio de Janeiro, Brazil*
[b]*NUCAT, COPPE, UFRJ, Rio de Janeiro, Brazil*

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INTRODUCTION

Hydrogenation of fatty acid is an important step of a larger catalytic fuel production process. These reactions can be catalyzed by molybdenum carbide (Mo_2C), an efficient catalyst cheaper than that based on transition metals. The overall triglyceride transformation proceeds into two steps[1]:

(i) thermal cracking of the triglyceride forming free fatty acids and
(ii) hydrogenation of the double bonds and of the carboxylic group of the free fatty acid forming n-alkanes.

There are two possibilities in the hydrogenation step, the reaction pathway by double bound addiction or by carboxylic group addiction. Moreover, the complete mechanism is unknown.

The aim of this work is obtain the reaction path for the hydrogenation step at Density Functional Theory (DFT) level on explicit carbide surface. For this study, acrylic acid was used as fat acid model.

METHODS

All calculation were made at DFT level with Generalized Gradient Approximation (GGA) functional PBE with periodic boundary condition (PBC). The energy cutoff for plane wave basis set was 410 eV.

For geometry optimization the projector augmented wave approximation was used and for the search for minimum energy path with nudged elastic band method (NEB) ultra-soft pseudo-potential approximation was used.

All geometry optimization, self-consistent field (SCF), density of states (DOS) and band energy calculation was done in Vienna Ab initio Simulation Package (VASP) and all NEB calculation were done in Quantum ESPRESSO suite of programs.

RESULTS AND DISCUSSION

Preliminary results show that the hydrogenation by oxygen atom in the carboxyl group is the most probable pathway, followed by dehydration. The activation energy is about 40 kcal/mol.

The pathway by addition to carbon 2 (see figure 1) is more likely than the pathway by carbon 3.

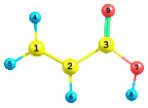

Figure 1. Acrylic acid structure and numeration.

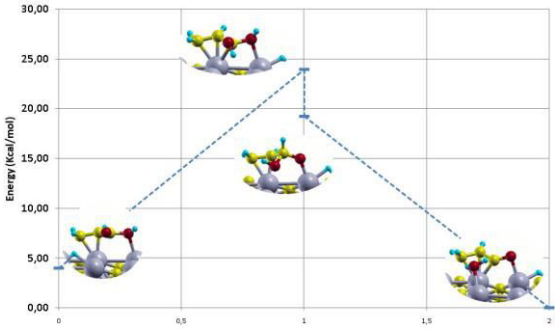

Figure 2. Hydrogenation by oxygen atom in the carboxyl group pathway.

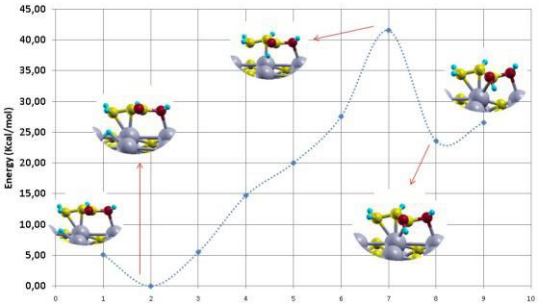

Figure 3. Minimum energy path for hydrogenation by oxygen atom in the carboxyl group obtained with NEB method.

CONCLUSIONS

The previous results show that the hydrogenation by carboxyl group is the most probable pathway for this step.

ACKNOWLEDGMENTS

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[1] L. A. Souza, J. L. Zotin and V. Teixeira da Silva, Appl. Catal. A, v. 449, p. 105-111, 2012.