

BIOFUEL PRODUCTION BY PHOTOCHEMICAL CRACKING OF VEGETABLE OILS EMPLOYING AROMATIC IMIDES SUPPORTED ON MESOPOROUS SILICATES AS SENSITIZERS

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Catalytic cracking is a key reaction in the petrochemical industry, allowing the conversion of high molecular weight hydrocarbons into low molecular weight fuel. Up to the years 1930, the cracking reaction was performed by thermal methods, but since then, with the introduction of the zeolites, which are microporous heterogeneous catalysts, catalytic cracking has become the most widely used

method. More recently, it has been recognized that catalytic cracking of vegetable oils could be used to obtain biofuel, as an alternative to the transesterification reaction. The use of photochemistry in cracking reactions, however, has remained largely unexplored. In the present proposal, the development of photochemical catalysis as a method for the cracking of vegetable oils will be pursued, using principles of nanotechnology to design nanostructured photocatalytic systems (Figure 1). For this goal, aromatic imides, such as phthalimides, 1,8-naphthalimides, 1,4,5,8-naphthalenediimides and 3,4,9,10-perylene diimides, will be employed as photosensitizers. Our group has great expertise in the photochemistry of these compounds. When excited by light, these compounds generate a variety of free radicals, which are expected to stimulate the cracking reaction, which is a radical chain reaction. The imides will be immobilized by covalent grafting onto the surface of silicates MCM-41 and SBA-15 (Figure 1), which are mesoporous nanostructured materials synthesized in the presence of surfactant micelles. The modified particles will be irradiated with a UV lamp and with natural sun light, in the presence of different vegetable oils. Mesoporous materials with different loads of the organic dye will be tested, containing either a single imide or a mixture of different imides.

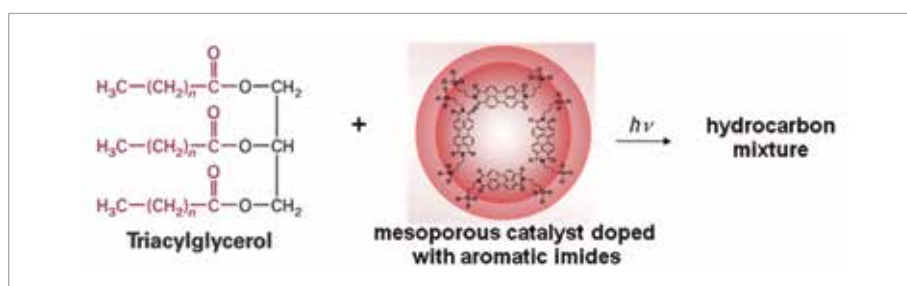


Figure 1. The concept of photochemical cracking of vegetable oils, showing a mesoporous catalyst with a perylene diimide sensitizer grafted into the inner pore walls

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The mesoporous heterogeneous catalysts doped with the photosensitizers were prepared by covalent grafting of the aromatic imides onto the walls of molecular sieves MCM-41 and SBA-15. Details of the synthesis and characterization of these materials are given in references 1-3. Cracking of a commercially available brand of soy oil in the presence of the new catalysts was first tested in the dark, in a thermogravimetric analyser (TGA) furnace, using 3 mg of soy oil and 0.1 mg of the mesoporous catalyst (*Figure 2A*). It can be observed that the soy oil, in the absence of catalyst, was cracked within the temperature range 400 - 500 °C. In the presence of the catalysts, on the other hand, the thermal degradation range was decreased to 350 - 450 °C, showing that the catalysts were active in the thermal cracking of the soy oil. In order to test the photochemical activity of the catalysts, however, it is necessary to drive the light beam inside the TGA oven. A system is being presently built that will allow irradiation of the samples inside the TGA oven.

Meanwhile, the performance of the heterogeneous photocatalysts under irradiation was evaluated using a standard system, namely the photodegradation of methylene blue (MB), a blue dye present in the effluents of the textile industry. When MB solutions were irradiated at room temperature with a 100 W Hg lamp (bandpass = 320 - 480 nm) in the presence of the heterogeneous photocatalysts, total mineralization of MB was observed after 5 h irradiation (*Figure 2B*). These results, which are presently submitted for publication, show the potential of the new catalysts in photodegradation reactions. The mesoporous catalysts were also effective in the photodegradation of asphaltenes isolated from petroleum.

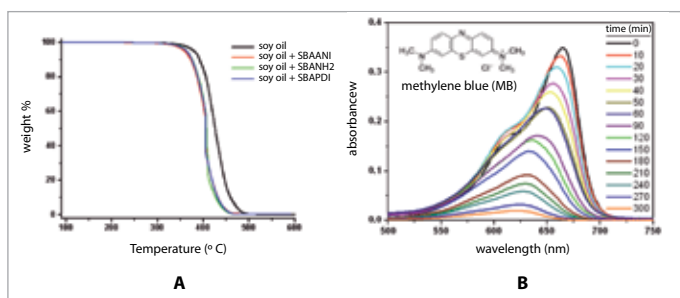


Figure 2. (A) Thermogravimetric analyses showing the cracking of soy oil in the presence and in the absence of the new catalysts. (B) Time-dependent absorption spectra for the irradiation of a MB solution in the presence of SBA-15 modified with 1,8-naphthalimide

MAIN PUBLICATIONS

Trindade FJ, Glauber JT, Fernandes ASA, Fernandes Jr. VJ, Silva BPG, Nagayasu RY, Politi MJ, Francisco L. Castro and Sergio Brochsztain. 2008. Covalent attachment of 3,4,9,10-peryleneimides onto the walls of mesoporous molecular sieves MCM-41 and SBA-15. *Microporous and Mesoporous Materials*. **113**: 463-471.

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Trindade FJ, Rey JFQR, Brochsztain S. 2012. Modification of molecular sieves MCM-41 and SBA-15 with covalently grafted pyromellitimide and 1,4,5,8-naphthalenediimide. *Journal of Colloid and Interface Science*. **368**: 34-40.

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