

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. 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, 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.

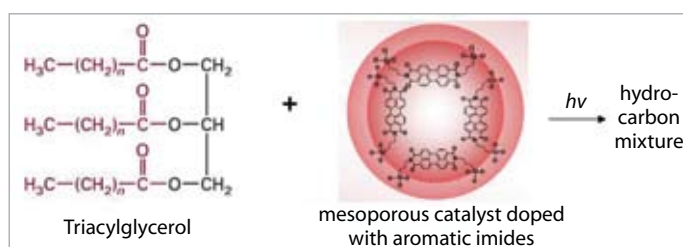


Figure 1. (A) Photographs showing the mesoporous catalyst MCM-41 before (left) and after (right) modification with the photosensitizer PDI. (B) Optical micrograph of the modified mesoporous catalyst, registered with an inverted fluorescence microscope, showing the strong red emission of the incorporated dye

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

In the first year of the project, the mesoporous catalysts doped with the photosensitizers were prepared by covalent grafting of 3,4,9,10-peryleneimides (PDI) onto the walls of molecular sieves MCM-41 and SBA-15. The mesoporous materials were first treated with 3-aminopropyltriethoxysilane (APTES) in anhydrous toluene, generating amine-containing surfaces. The amine-containing materials were then reacted with 3,4,9,10-perylenetetracarboxylic dianhydride (PTCA), generating surface-grafted PDI. The samples showed the red color which are typical of the PDI dyes (*Figure 1A*). The new materials, designated as MCMPDI and SBAPDI, presented absorption and emission spectra corresponding to weakly coupled PDI chromophores, in contrast to the strongly coupled rings usually found in solid PDI samples. The materials showed a red fluorescence, which could be observed by the naked eye under UV irradiation or with a fluorescence microscope (*Figure 1B*). The next step is the test of the catalytic activity of the new materials for the cracking of vegetable oils, using a thermogravimetric analyzer coupled with mass spectrometer. This system allows *in situ* analysis of the hydrocarbon mixture obtained after thermal degradation of the oil. The system will be tested in the dark and under UV irradiation.

Graphical abstract. Catalytic cracking of vegetable oils by a mesoporous catalyst doped with an aromatic imide



MAIN PUBLICATIONS

Trindade FJ, Fernandes GJT, Araújo AS, Fernandes Jr. VJ, Silva BPG, Nagayasu RY, Politi MJ, Castro FL, Brochsztain S. 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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