

Michelle N. Chrétien Ph. D.

NSERC Post-doctoral Fellow

CONCORDIA UNIVERSITY • DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
• 7141 SHERBROOKE STREET WEST • MONTRÉAL, QC, H4B 1R6 • (514) 848-2424
x5324 • EMAIL: mnchreti@vax2.concordia.ca

ESSAY

Zeolites are inorganic solids that are closely related to the soil, sand, minerals, and clays that make up much of the earth around us. Zeolites are nanoporous, crystalline aluminosilicate materials and their tertiary structure forms a series of strictly uniform channels and cavities of molecular dimensions that are repeated along the tri-directional structure of the lattice.

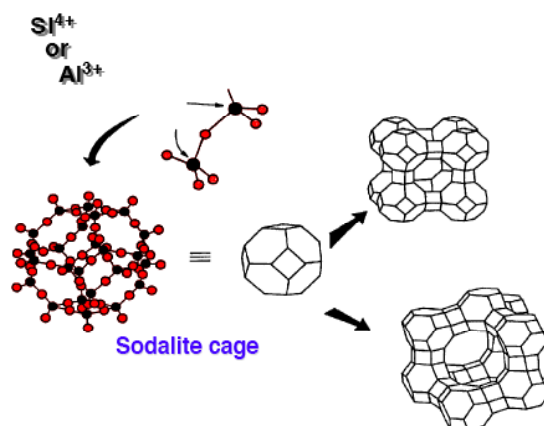


Figure 1. Representation of the $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra that are the primary building blocks of zeolites, as well as the sodalite *periodic building unit* and zeolites A, X, and Y.

Although the use of zeolites in crude oil conversion and detergent formulations has been extensively studied over the past four decades, the interest of photochemists in zeolites as host systems for supramolecular photochemistry is relatively recent. Zeolites have emerged as convenient and versatile solid hosts for the control of photochemical and photophysical processes. At the time of initiating graduate studies I was very interested in exploiting zeolites, which are inexpensive and readily available, to prepare new materials having interesting and valuable properties. Accordingly, I became

involved in several projects exploring the photochemical and photophysical properties of new materials, prepared by the encapsulation of organic or organometallic species within the cavities of aluminosilicate zeolites. Along the way we have examined different facets of intrazeolite photochemistry with the additional aim of developing a more profound understanding of how zeolite media can influence the behaviour of encapsulated guests.

Our research in the area of zeolite photocatalysis was inspired by the profoundly important need for efficient and economical methodologies for the purification of drinking water. In 2004, UNICEF estimated that over one billion people were still without access to sanitary drinking water. The rate of natural biological remediation is surpassed by the quantity of waste released into the system and the vulnerability of global fresh water resources is becoming increasingly apparent. To cope with the effects of pollution on the hydrosphere, the development of treatment methodologies based on efficient catalytic materials has become increasingly important.

Photocatalysts are superior to thermal catalysts in many respects, however, there are still several disadvantages associated with the use of traditional photocatalysts for large-scale remediation. For example, TiO_2 , a popular heterogeneous catalyst for wastewater purification does not have significant absorption beyond 370 nm therefore requiring UV light for efficient photodegradation. The advantages of alternative photocatalytic systems operating under visible-light illumination are obvious. We have designed zeolite-based photocatalytic materials by taking advantage of the zeolite framework to prepare a multi-component system comprising a semiconducting oxide and an electron-accepting or -donating dye.

Ultraviolet irradiation of TiO_2 results in the generation of reactive oxygen species, ultimately causing the photodegradation of various biological and organic materials. To harness solar energy more efficiently, the zeolite matrix was used to combine TiO_2 with a highly-coloured dye in order to produce the same reactive species via a visible-light-induced, electron transfer interaction. The electron transfer nature of the interaction in these materials was thoroughly characterized by steady-state and time-resolved spectroscopy and the catalytic behaviour was examined with respect to

the photodegradation of a model biological substrate. We observed that our material combining TiO_2 and 2,4,6-triphenylpyrylium was more active than TiO_2 anatase, a popular commercial photocatalyst. The development of water-purification catalysts for use in combination with solar radiation is an important direction in the pursuit of an economically viable solution for wastewater remediation.

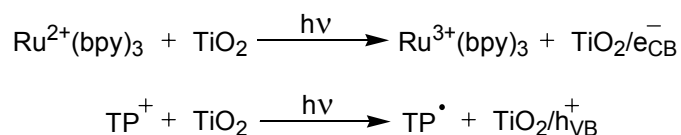


Figure 2. The products of photoinduced electron transfer between TiO_2 and the two dyes, tris(2,2'-bipyridine)ruthenium(II) and 2,4,6-triphenylpyrylium cation.

In the course of our research, zeolite materials have also been used in a more traditional sense as matrices for the stabilization of various transient or reactive species. In our investigation of the photochemistry of ketoprofen (a non-steroidal anti-inflammatory drug), this drug was observed to undergo an intrazeolite photodecarboxylation to generate a benzylic carbanion. The lifetime of the zeolite-encapsulated carbanion was found to be fifty times longer than in aqueous solution! This provided the first example of a carbanionic species stabilized by zeolite encapsulation, disabusing the widely accepted notion that zeolites are ineffective hosts for reactive, negatively-charged species.

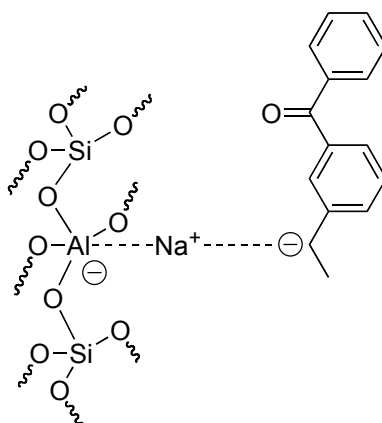


Figure 3. Schematic representation of a possible carbanion stabilization mode in NaY.

The enhanced lifetime allows intermolecular nucleophilic addition chemistry to compete with protonation, the dominant reaction in aqueous solvents, and a photo-

initiated, carbon-carbon bond forming reaction was observed. In addition, the observation of nucleophilic addition products from the irradiation of ketoprofen in the presence of various nucleophiles supports the assignment of this reactive intermediate as the ground state singlet carbanion. The nature of this intermediate cannot be uniquely confirmed spectroscopically and its identity and has been contested in the literature in the past.

We have also investigated the feasibility of elaborating traditional sunscreens based on the novel concept of encapsulation, this work was aimed at preventing the side-effects that are common with many commercial sunscreens. Significant evidence exists that over-exposure to solar radiation has a negative impact on human health. Skin cancer is the most commonly occurring cancer in Canada, accounting for one third of all newly diagnosed cancers and over one million people in Canada and the USA are diagnosed with melanoma, basal cell, and squamous cell cancers each year.

With increased awareness of the relationship between radiation exposure and skin cancer, the use of sunscreens has exploded. Sunscreens have become ubiquitous, appearing in a surprising number of products ranging from shampoo to lipstick. With this increase in usage has come an accompanying increase in the reported occurrences of photoallergy and phototoxicity; it is currently estimated that *ca.* 20% of the population are photosensitive to one or more sunscreen active ingredients.

Increasing reports of photosensitivity, and commercial formulations containing mixtures of components whose interactions are largely uninvestigated, pushed us to pursue a solution to problems associated with current commercial sunscreens. We reasoned that encapsulation of sunscreen active ingredients in a suitable host might effectively prevent interaction with biological substrates, while at the same time preserving the desirable scattering/absorbing properties of the filter. Through zeolite encapsulation we hoped to obtain a *supramolecular sunscreen* that would retain the beneficial characteristics of the parent sunscreen but prevent photosensitivity by eliminating contact between sunscreens and skin components, as well as eliminating interaction between ingredients.

There are numerous intrinsic advantages to this strategy. The aluminosilicate framework is transparent in the mid-UV, enabling the encapsulated sunscreen to absorb radiation and, due to the particulate nature of zeolites, the supramolecular sunscreens will act as light scatterers, eliminating the need for semi-conductor oxides (which are employed with increasing frequency) in topically applied products .

In the course of this work several important aspects of sunscreen photochemistry were brought to light. We have shown that the common combination of metal oxide scatterers with soluble organic absorbers results in the light-induced destruction of the latter. Surprisingly, this process was accelerated in the presence of surfactants, which are commonly considered “non-active” ingredients in sunscreen formulations. Also surprisingly, in light of their solution photostability, several popular sunscreens were observed to induce cell mortality and DNA damage in human skin cells. Encapsulation of sunscreens in zeolites prevented the metal oxide-induced photodegradation as well as the deleterious effects with respect to human skin cells while offering photo-protection that is comparable to classical or “naked” sunscreens.

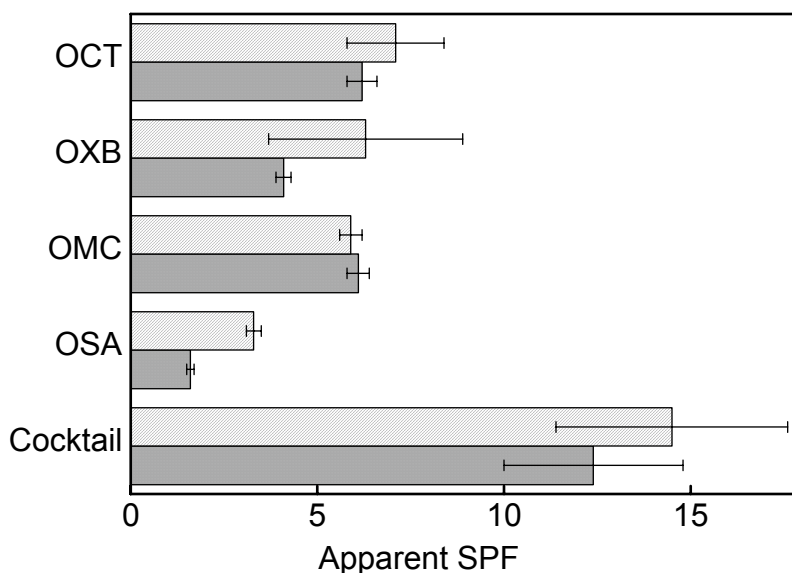


Figure 4. *In vitro* SPF values determined using the Labsphere UTA for equivalent amounts of five popular free (stripes) and encapsulated (grey) sunscreens suspended in ethylene glycol. The cocktail contained equal amounts of all four free or encapsulated sunscreens.

In total, our work represents a significant contribution to the general area of supramolecular photochemistry while at the same time providing new materials that may, hopefully, contribute to improving human health.