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Zeolite-coated quartz fibers as media for photochemical and photophysical studies

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Zeolite-coated optical fibers are useful as media to carry out asymmetric photochemical reactions and for sensing polyaromatic compounds.

Among the several organized assemblies (cyclodextrins, host–guest complexes, micelles, liquid crystals, crystals, silica, clay, and zeolites) that have been explored as media for photochemical reactions, zeolites have been found to be more general and useful.[1,2] This is mainly because zeolites accommodate a variety of reactant molecules and permit the occurrence of a number of reactions. In spite of these advantages, the experimental difficulty of uniformly exposing all guest molecules included in zeolites has been a deterrent for those wishing to use them as reaction media. For example, exposure of zeolite powders to light results in the excitation of molecules present only on the outer layers of the powder and create dark region within interior of the sample. We have overcome this problem by the use of a zeolite–hexane slurry.[3] Recently, fiber optics has been established to enable transmission and distribution of light to active sites such as supported TiO_2, sol–gels or organic polymers much more effectively.[4] This prompted us to explore the use of zeolite immobilized optical fibers as a way to overcome the problem of uniform exposure during photochemical reactions. In this report we present results of our studies exploring the use of zeolite immobilized optical fibers as media for asymmetric photoreactions and for sensing aromatic molecules through their phosphorescence.

Quartz fibers immobilized with Y zeolite particles were prepared by following literature procedure.[5] In a typical experiment, silica sol (prepared by adding 0.713 g of tetraethyl orthosilicate and 0.5 mL of 0.06 M HCl to 4.0 g of ethanol) was added drop wise to a stirring solution of 0.4 g of bare quartz fibers[6] in 20 mL of ethanol. After equilibrating for 12 h, the mixture of silica sol and quartz fibers was heated at 70 °C to dryness. The silicate coated quartz fibers were dip coated with a slurry of 0.5 g of NaY, or LiY zeolite, and 15 mL of ethanol. Annealing of zeolite particles was carried out first by drying the fibers at 70 °C in a vacuum oven and then calcining at 480 °C in air for 12 h. The scanning electron micrograph images of the bare and NaY zeolite coated quartz optical microfibers provided in Fig. 1 indicate that zeolite particles are immobilized on the external surfaces of the fiber.

The feasibility of zeolite immobilized optical fibers as media for asymmetric induction was tested by using three independent photochemical reactions as probes (Scheme 1): (a) photoreduction of phenyl cyclohexyl ketone **1a**,[7] (b) geometric isomerization of *S*-(−)-1-phenylethylamide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid **2a** and (c) oxadi-π-methane rearrangement of *R*-(+)–1-phenylethylamide of 2,6,6-trimethylcyclohexa-2,4-dienone-4-carboxylic acid **3a**.[9] Irradiation of **1a** either in solution or within NaY yields the Norrish type II product **1b** only. However, irradiation of **1a** (7 mg) and (+)-pseudoephedrine (26 mg) included in NaY (300 mg) zeolite as a hexane slurry gave **1c** and **1d** as the main product in 35% ee. Irradiation of the above mixture in solution (in the absence of zeolite NaY) gave racemic **1c** and **1d**, with **1b** being the major product. To test the viability of NaY coated quartz fibers as reaction media, the chiral inductor (+)-pseudoephedrine (20 mg) and the reactant **1a** (5 mg) were adsorbed onto the NaY coated fiber (total weight: 500 mg, weight of NaY adsorbed: 170 mg) by soaking all three in methylene chloride–hexane solution for 12 h. The fibers were removed from the solution, washed with hexane, and dried at 65 °C under reduced pressure (10^{-3} Torr). The dry fibers were irradiated for 90 min and products were extracted by soaking the irradiated fibers in acetonitrile for 8 h. The products were analyzed by GC (Supelco β-dex-350–OV 1701 custom-made column). Similar to NaY–hexane slurry irradiation, the intermolecular reduction products **1c** and **1d** were formed as the main products in 45% ee. Thus the product distribution as well as ee obtained were nearly the same both during NaY–hexane slurry and NaY coated fiber irradiations.

Similarity between NaY–hexane slurry and NaY–coated fiber was further established with photoisomerization of **2a** and photorearrangement of **3a** (Scheme 1). Typically, 3 mg of the reactant and 300 mg of zeolite powder were used for slurry irradiations while 2 mg of the reactant adsorbed on 500 mg of zeolite immobilized optical fibers (weight of NaY: 170 mg) were used for fiber irradiations. The analyses of the products were carried out with the help of GC (SE-30 column). Irradiation of *S*-(−)-1-phenylethylamide of 2β,3β-diphenylcyclopropane-1α-carboxylic acid **2a** in hexane–methylene chloride solution gave the *trans* isomers **2b** and **2c** in 2% de. Irradiation of the same molecule included in LiY and NaY (2 mg of reactant in 300 mg of zeolite) gave the *trans* isomers in 80% (B) and 28% (A) de. Irradiation (90 min) of **2a** adsorbed on LiY and NaY coated quartz fibers gave **2b** and **2c** in 77% (B) and 33% (A) de respectively, results similar to those during

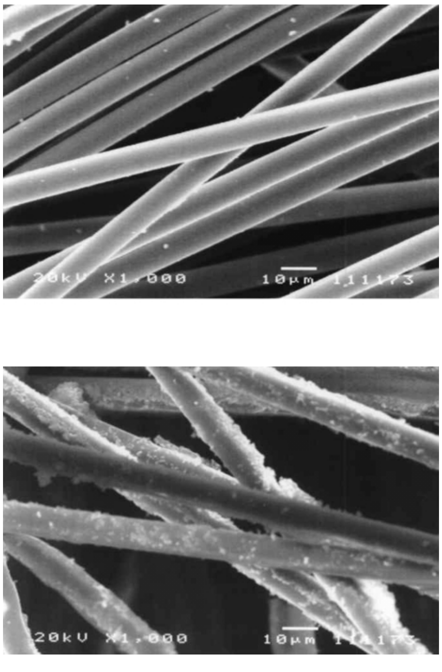

Fig. 1 Scanning electron micrograph of bare optical fibers (top) and zeolite coated optical fibers (bottom).

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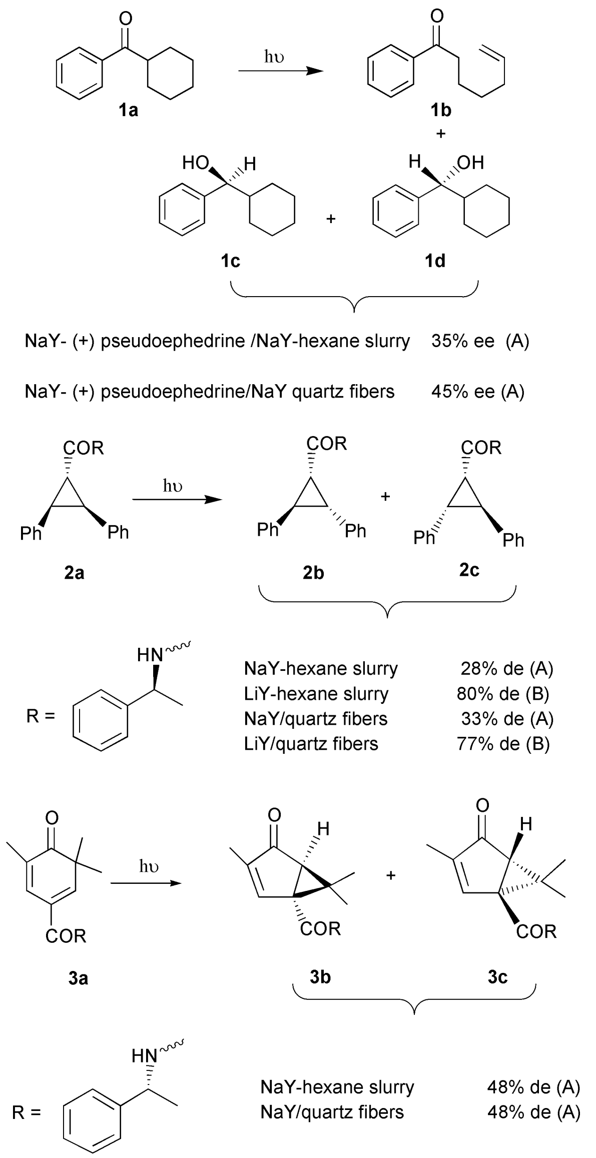

Scheme 1 The isomer that is obtained in excess is marked as A and B in parenthesis. The first peak that elutes on the GC or HPLC is arbitrarily marked as A.

zeolite–hexane slurry irradiations. Upon excitation of **3a** in trifluoroethanol solution, the rearrangement products were obtained in 5% de (B). In stark contrast to the solution behavior, irradiation of **3a** included in NaY as hexane slurry gave the products **3b** and **3c** in 48% de (A). The de obtained upon irradiation of **3a** included in NaY coated quartz fiber was also 48% (A) (10 min irradiation). In all the above three examples, the fact that control experiments with silica-coated optical fibers did not result in de or ee emphasizes the importance of the zeolite in this operation.

The above three examples demonstrate that zeolite coated optical fibers could be used to achieve chiral induction during photochemical transformations. Advantages in using quartz coated fibers over NaY powders are the following: (a) the fiber method allows exposure to light of almost all molecules included in NaY. (b) Zeolite coated fibers could be reused at least three times without reactivation (the coated fibers were heated at 120 °C at 10^{-3} Torr pressure to remove the solvent acetonitrile used during extraction of the reactants and products). For example geometric isomerization of **2a** over LiY coated optical fibers gave the *trans* isomer in 79%, 77% and 76% de during the first, second and third cycles. (c) The fiber method allows for scaling up of the photoreaction if needed.

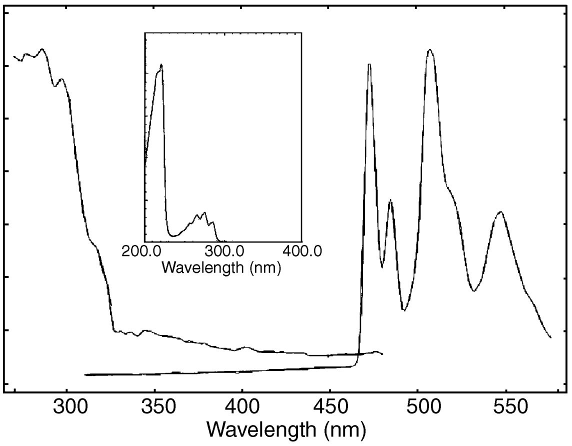

Fig. 2 Emission spectra (excitation 290 nm) and excitation spectra (emission 500 nm) at 77 K of naphthalene included in TlY coated optical fibers. (Corning Glass O-52 cut-off filter was used). The absorption spectra of naphthalene in hexane is shown in the insert.

Having established that zeolite immobilized optical fibers are suitable for carrying out photochemical reactions, we tested their use for photophysical studies. Fig. 2 presents the emission spectra of naphthalene loaded in TlY (approximately 1 molecule per 5 supercages) coated optical fibers. The spectrum is similar to that observed using TlY zeolite powder.[10] As expected only phosphorescence was observed. Our results indicate that Tl-exchanged zeolite immobilized optical fibers have potential as an efficient and inexpensive method for real-time, selective chemical sensing.

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