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Shape-Selective Photosensitized Isomerization of Stilbene Using a Benzophenone Incorporated Within Acid Zeolites

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Abstract: A series of heterogeneous photosensitizers has been obtained by immobilization of 4-aminobenzophenone (ABP) within acid zeolites of medium and large pore size. The strong interaction between the amino substituent of ABP and the acid sites of the zeolite is revealed by the red-shift (ca. 50 nm) of the long wavelength absorption band in the UV/Vis spectra of the composites. ABP when included within HZSM-5 (ABP-HZSM-5) behaves as the first shape-selective photosensitizer. Thus, trans-stilbene could be photochemically isomerized to cis-stilbene in the presence of ABP-HZSM-5, while the reverse cis to trans isomerization failed. According to the relative dimensions of the zeolite hosts, ABP incorporated within HY, Hβ and HMOR showed no remarkable difference in the isomerization efficiency of both stilbene isomers.

It has been reported that the cis-trans photostationary mixture of stilbene can be controlled by performing the direct photolysis in the presence of medium and large pore zeolites,[1-3] the most dramatic case being ZSM-5 and silicalite. Owing to the molecular sieves properties of these pentasil zeolites, trans-stilbene (TS) can be readily incorporated within the tridirectional channel systems of these solids (straight 5.2x5.7 Å, sinusoidal 5.3x5.6 Å), while by contrast the different molecular dimensions precludes the cis isomer (CS) to penetrate inside the internal voids of these medium pore zeolites. When irradiating, the tight fit of the pentasil reaction cavity prevents adsorbed TS from C=C double bond isomerization, while CS in the liquid phase can freely undergo the photochemical isomerization to TS. This amazing discrimitation between the two stilbene stereoisomers can even be successfully exploited to obtain pure CS by removing it from the last traces of TS.[4] The remarkable shape-selectivity displayed by ZSM-5 is not unprecedented and lies on the basis of some industrial applications of this zeolite as catalyst for the synthesis of p-xylene and other alkylaromatics.[5-7]

In the present communication we want to show that it is possible to achieve just the reverse situation, i.e. essential lack of isomerization from CS and exclusive irradiation of TS, by performing the photosensitized version of this reaction using a benzophenone previously incorporated within ZSM-5. Comparison with other large pore zeolites with mono as well as tridirectional topology reveals that this result is exclusively attributable to the unique shape-selective characteristics of ZSM-5.

In order to define a reaction cavity[8] essentially stationary, constant and time-independent, where cavity/size control by the zeolite lattice could be operative, entrapment and immobilization of the sensitizer was considered a necessary prerequisite. This goal was accomplished by adsorbing 4-aminobenzophenone (ABP) onto acid zeolites. It was anticipated that the weak basic nature of the amino group will interact with the sites of the H$^+$-form of the zeolites.

The corresponding acid zeolites (HY100, Hß and HMOR and HZSM-5) were prepared according to reported procedures [9] and their acidity measured by the pyridine adsorption-desorption method.[10] Incorporation of the sensitizer was carried out by stirring at 90 °C for 1 h a suspension of ABP in isooctane and the zeolite previously dehydrated (500 °C, overnight). The composites were submitted to exhaustive solid-liquid extraction using CH_2Cl_2. Finally, the yellow samples were pumped out and stored without any special precaution.

A large portion of the initial ABP (typically about 2-4 wt% of the resulting material) was strongly retained by the zeolites and could not be recoverable by extraction. The composites were characterized by thermogravimetric analysis-differential scanning calorimetry, FT-IR, diffuse reflectance, and luminescence spectroscopy. Interestingly, it is known[11] that the long-wavelength absorption band in the UV spectrum of ABP exhibits a bathochromic shift after protonation. As it is illustrated by Figure 1 for the case of the ABP-HZSM-5 sample, analogous red-shift was observed in the UV/Vis diffuse reflectance when ABP is incorporated within the zeolites studied, indicating a strong interaction between the NH_2 substituent of ABP and the acid sites of the zeolites.

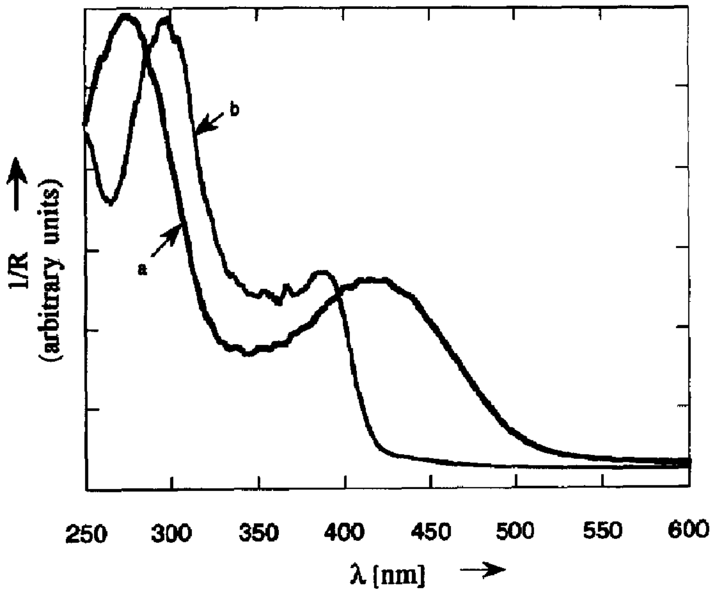
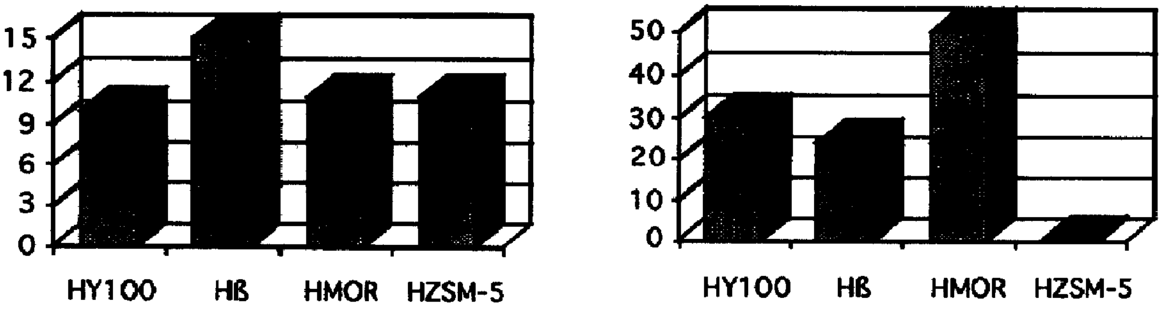


Fig.1. Diffuse Reflectance (1/R, inverse of reflectivity) of ABP-HZSM-5 (a) and ABP (b).

The results attained in the simultaneous long-wavelength irradiation ($\lambda \geq 350$ nm) of TS and CS in CH_2Cl_2 under Ar, in the presence of ABP entrapped within the zeolites studied are presented in Fig. 2.

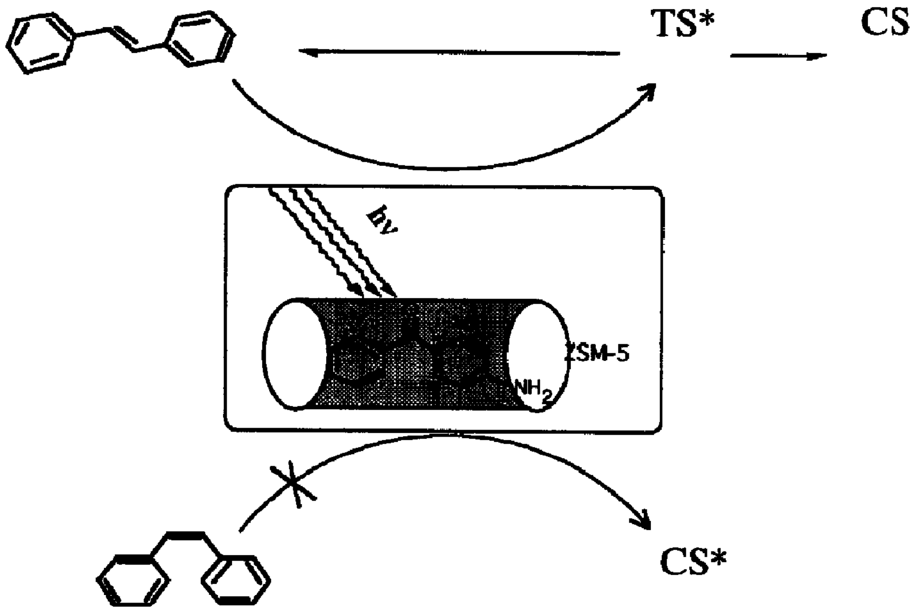


A B

Fig. 2. Results of the photochemical isomerization of stilbene sensitized (λ≥350 nm) by ABP adsorbed within different zeolites. A: yield of CS upon irradiation of TS for 3 h; B: yield of TS upon irradiation of CS for 1 h.

What is important from this data is that while the set of zeolites exhibits similar initial activity for the TS to CS isomerization (Fig.2A.), no significant conversion was observed for the CS photolysis in the presence of ABP-HZSM-5. For this experiment, much longer irradiation times only led to very low conversions (≤3 %). As far as we know this constitutes the first example of a shape-selective photosensitized reaction.

This result can be easily interpreted assuming that ABP is well protected by the ZSM-5 lattice and not accessible to CS (Scheme 1). Moreover, since isomerization of TS can only takes place outside the channels of the ZSM-5, excited TS must be able to diffuse to the liquid phase, therefore suggesting that the active population of ABP must be predominantly located close to the pore openings and not deeply within the micropores.



Scheme 1. Shape-Selective photosensitized isomerization of stilbene using ABP incorporated within ZSM-5.

In the case of ABP-HMOR composite, a photostationary mixture starting from TS or CS not much different to that achieved in the CH_2Cl_2 homogeneous ABP experiment or to those reported for typical energy transfer photosensitizers could be obtained.[12] However, for the TS isomerization in the presence ABP-HZSM-5 sample, the isomerization apparently stopped while the mixture is still far from the corresponding stationary value.[13] This fact can be related with a progressive deactivation by blockage of the small micropores of ZSM-5. In fact, reuse of the ABP-HZSM-5 sensitizer without any treatment led to a appreciable decrease (about 10%) in the TS isomerization efficiency.

In conclusion, we have shown that the activity of a typical energy transfer sensitizer can be controlled by incorporation within zeolite hosts of different topologies. Acid-base interaction between the zeolite sites (overwhelmingly located on the internal surfaces) and the substituent NH_2 group has been found strong enough to immobilize the photosensitizer during the photochemical reaction. This has allowed for the first time to observe a shape selectivity in a sensitized photochemical reaction.

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13. The maximum yield of CS that could be obtained for the TS isomerization photosensitized by ABP-HZSM-5 was 52%.

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