

Short communication

## A novel and efficient photocatalyst: TiO<sub>2</sub>-HZSM-5 combine thin film<sup>☆</sup>

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### Abstract

Thin films containing TiO<sub>2</sub>/HZSM-5 are found to be more active for the photocatalytic degradation of phenolic wastewaters than films without zeolite. The optimum ratio of TiO<sub>2</sub>/HZSM-5 is found to be 1/4. The presence of zeolite increases the concentration of substrate near the photocatalyst and protects the organic support against the photodegradation.

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The use of immobilized photocatalysts is gaining importance in the elimination of pollutants from wastewaters. Many methodologies were reported for the immobilization of the TiO<sub>2</sub> photocatalyst on solid supports like clays, zeolites, glass, quartz, silica, activated carbon, fiberglass, etc. [1] and pumice stone [2]. Immobilization of TiO<sub>2</sub> is commonly reported to reduce its photoactivity [3]. Our recent work on TiO<sub>2</sub>/zeolites and TiO<sub>2</sub>-zeolite combine [4] in slurry demonstrated that supporting TiO<sub>2</sub> without interaction is showing enhanced photodegradation. Such a synergism is seen due to the adsorption properties of the support pooling the pollutant molecules and facilitating the photodegradation activity of TiO<sub>2</sub> more effectively. In continuation of our earlier studies on TiO<sub>2</sub>-zeolite combine slurry systems it has been desired to develop a novel thin film combine system for treating wastewaters. Polyethylene sheets [5], polystyrene beads [6], cellulose microspheres [7], polyvinyl acetate [8], polyvinyl chloride [9] and fluoropolymer resins [10] are employed for immobilization of TiO<sub>2</sub>. The stability of polymers to UV light irradiation remains

as the major constraint in the preparation of polymer based films.

In the present investigation, UV light resistant material like acrylic polymer associated with zeolite is used for the making TiO<sub>2</sub>-based thin films for photocatalytic applications. In this communication, we report the preparation of titania-zeolite combine thin film as an active photocatalytic system for the first time to the best of our knowledge. The method involves the immobilization of preformed TiO<sub>2</sub> and TiO<sub>2</sub>-HZSM-5 combine into flexible films by a simple spray technique using acrylic emulsion (AE) at ambient conditions. The process of TiO<sub>2</sub> immobilization in general is carried out by various organic titania precursors that require high thermal treatment. In contrast, the films prepared here are used directly without any thermal pretreatment.

Thin film photocatalysts were prepared with TiO<sub>2</sub> Degussa P25 (anatase/rutile 70/30, particle size 30 nm, BET surface area 55 m<sup>2</sup> g<sup>-1</sup>) and HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30, PQ Corporation, The Netherlands). TiO<sub>2</sub> and HZSM-5 of known wt.% films are made with a proprietary binder using a spray technique onto an inert support (tile) [11]. The film can be easily separated by simply suspending the tile in water after spraying the mixtures. The separated films were in the form of a sheet containing photoactive TiO<sub>2</sub> particles along with HZSM-5 adsorbent. Bare acrylic emulsion

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(AE), HZSM-5-acrylic emulsion (Zeo-AE), TiO<sub>2</sub>-acrylic emulsion (Ti-AE) and TiO<sub>2</sub>-HZSM-5-acrylic emulsion (Ti-Zeo-AE) films were made. Their respective photocatalytic activities for phenolic wastewaters were evaluated and the data were compared. The UV lamp used for the photocatalytic experiments is a high pressure mercury lamp emitting wavelengths longer than or equal to 254 nm. Photocatalytic transformation of phenol with combine photocatalysts was also observed in sunlight, but it is a little slower and not quantitatively so reproducible.

The diffraction patterns of the films were recorded with Siemens D-5000 X-ray diffractometer using Cu K $\alpha$  radiation at a scan rate of 0.09° (2 $\theta$ ) s<sup>-1</sup>. TiO<sub>2</sub> and TiO<sub>2</sub>-zeolite thin films were observed in Hitachi S-520 Scanning Electron Microscope and the samples were mounted on aluminium using double-sided adhesive tape coated with gold in HUB-SGB vacuum coating unit. The photocatalytic degradation of phenol was monitored by HPLC using C<sub>18</sub> column, UV detector ( $\lambda = 220$  nm) and methanol/water of ratio of 50/50 (v/v) as the eluent with a flow of 1 ml min<sup>-1</sup>.

Fig. 1 shows the XRD patterns of different thin films prepared for photocatalytic evaluations. The XRD of composite film (Fig. 1d) compared with that of bare polymer film (Fig. 1a) shows that the method employed in this investigation to spray mechanically mixed TiO<sub>2</sub> + zeolite + polymer emulsion distributed TiO<sub>2</sub> and zeolite on the surface of the polymer. On combining polymer either with HZSM-5 (Fig. 1b) or TiO<sub>2</sub> (Fig. 1c) or with both (Fig. 1d) anatase and HZSM-5 phases are predominantly observed, whereas the structure of acrylic polymer do not appear. A thorough examination of the SEM photographs leads to the follow-

ing remarks. A bare acrylic emulsion film (Fig. 2a) shows highly uniform morphology of a polymer with small and large characteristic voids with a reticulate network. This uniformity is slightly disturbed with the incorporation of HZSM-5 (Fig. 2c) onto the polymer network. Whereas the uniformity of the polymer network is unaffected on dispersing TiO<sub>2</sub> particles and it is easily distinguished against a polymer background (Fig. 2b). The morphology of the final composite film being a mixture of TiO<sub>2</sub>, HZSM-5 and acrylic emulsion appears totally different (Fig. 2d), which might be due to the difference in the size of the particles. All the films appeared physically similar to naked eye, but the morphological differences are highlighted through SEM.

Prior to the start of photocatalytic experiments, adsorption (dark) experiments were carried out for a period of 1 h on a coated ceramic tile of size (10 cm  $\times$  10 cm) suspended horizontally in 200 ml of phenol solution (10<sup>-4</sup> M) taken in a wide beaker and the solution is in continuous stirring by placing in a shaking unit. Before starting the photocatalytic experiments, it is necessary to optimize the amount of zeolite as well as TiO<sub>2</sub> to obtain an efficient photocatalyst. When 200 ml of phenol 10<sup>-4</sup> M was used 45% of phenol is adsorbed on 400 mg of zeolite-acrylic films. Our earlier studies [4] also show that about 40–50% adsorption (dark experiment) on zeolites is ideal to differentiate adsorption from photodegradation. Fig. 3 shows the effect of variation of TiO<sub>2</sub> amount in composite Ti-Zeo-AE film for phenol degradation. It is clear that about 25 wt.% of TiO<sub>2</sub> with respect to zeolite is the best condition to achieve the synergism between TiO<sub>2</sub> and HZSM-5. This synergic effect may be due to the fact that the presence of zeolite prevents the

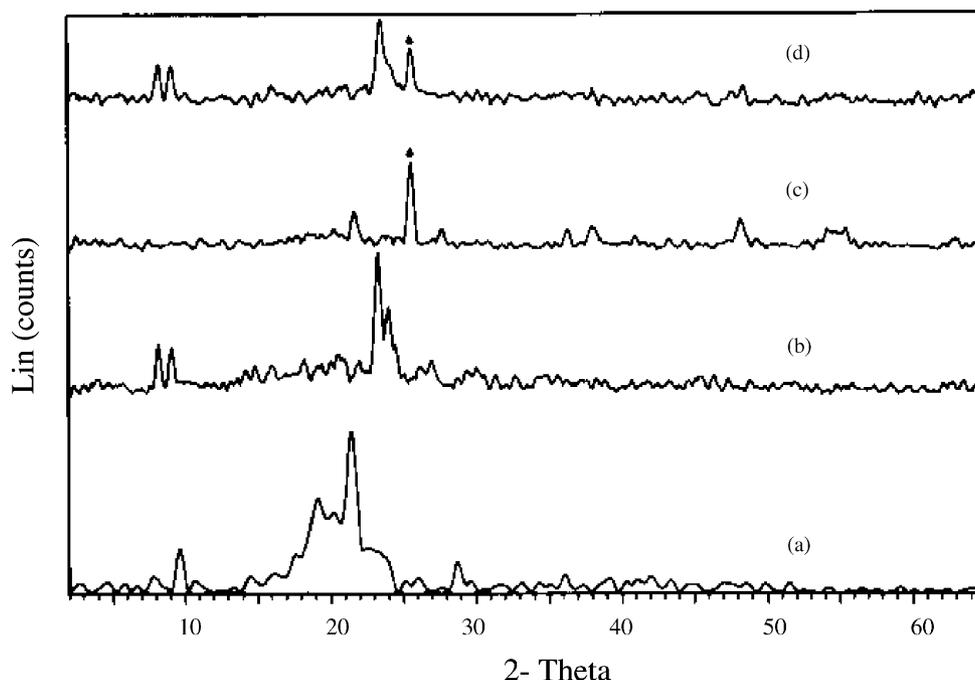


Fig. 1. X-ray diffraction patterns of (a) AE, (b) Zeo-AE, (c) Ti-AE and (d) Ti-Zeo-AE films. (▲) Characteristic 'd' lines of anatase of TiO<sub>2</sub>.

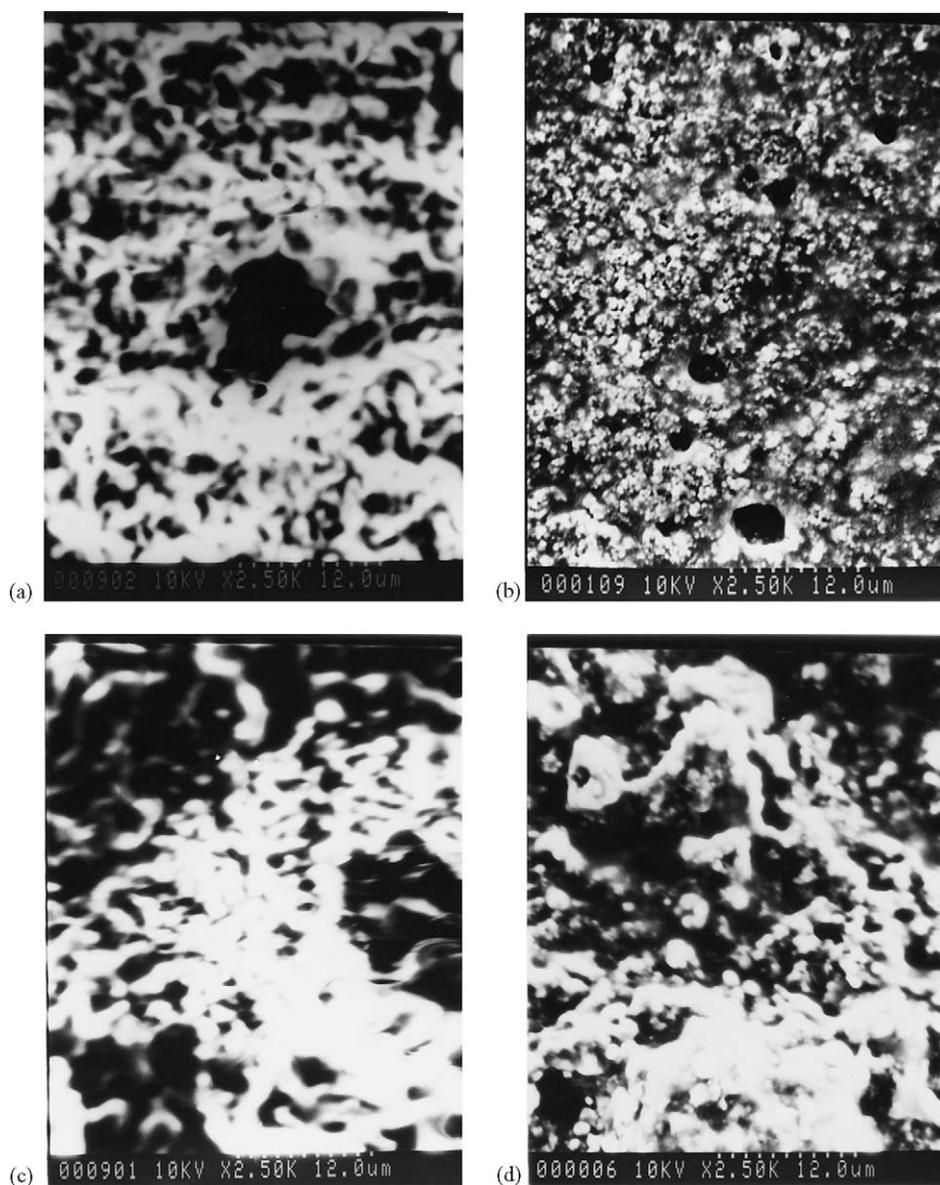


Fig. 2. Scanning electron micrographs of initial films (a) AE, (b) Ti-AE, (c) Zeo-AE and (d) Ti-Zeo-AE films.

reaction of reactive species formed on  $\text{TiO}_2$  with the polymer (isolation effect) and by maintaining the substrate near the photocatalyst (local concentration effect) as depicted in Scheme 1. Fig. 4 clearly highlights the dark and light experiments of phenol degradation over AE, Zeo-AE, Ti-AE and Ti-Zeo-AE films. The enhanced photocatalytic activity over the composite Ti-Zeo-AE film is reflecting the beneficial adsorption properties of HZSM-5. In the absence of HZSM-5, Ti-AE film (Scheme 1a) is not efficient for photocatalysis and thus the presence of an adsorbent is proved to play a positive role to make the photocatalytic films highly active (Scheme 1b). This is also confirmed from TOC results, wherein the composite film shows less TOC compared to the only Ti-AE films. The composite films show stable activity for long UV light exposure. For comparison a solution

of phenol of the same concentration was irradiated in the same device, but in the presence of  $\text{TiO}_2$  in slurry  $0.25 \text{ g l}^{-1}$ . The reaction rate was approximately three times faster than with the combine film, as it is partly due to the fact that the surface exposed to the light is more in the slurry. The loss of efficiency is not so high and it is largely compensated for the advantage of the elimination of filtration. It was also experimentally proved that the photocatalytic degradation rate of phenol with composite catalyst had the same order of magnitude in sunlight as with artificial UV light used in the present study.

The formation of products was also investigated. In all cases the main products identified were: benzoquinone and hydroquinone. With the combine thin films benzoquinone was the main product and with the  $\text{TiO}_2$  films hydroquinone

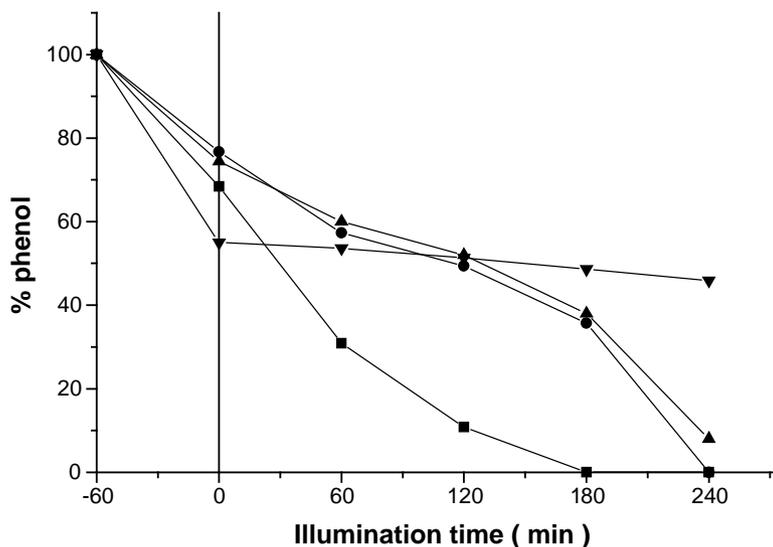
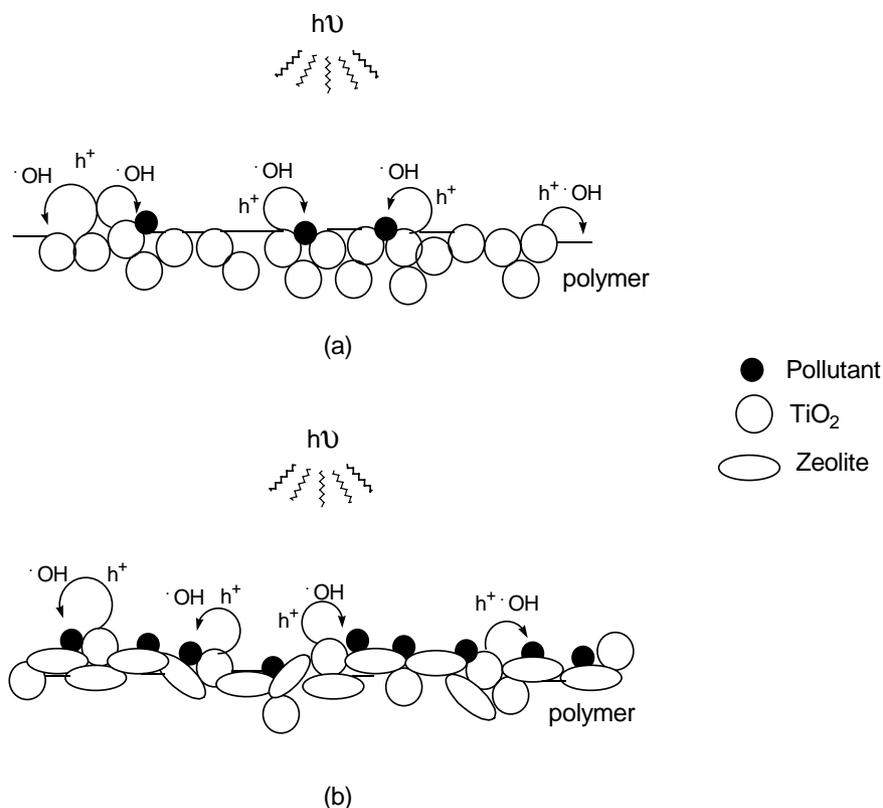


Fig. 3. Influence of TiO<sub>2</sub> on TiO<sub>2</sub>-HZSM-5-acrylic composite films for photocatalytic degradation of phenol (10<sup>-4</sup> M). In all samples 400 mg of zeolite was used for 1 ml of acrylic emulsion. (▼) TiO<sub>2</sub>/HZSM-5 (0/400); (■) TiO<sub>2</sub>/HZSM-5 (100/400); (●) TiO<sub>2</sub>/HZSM-5 (200/400); (▲) TiO<sub>2</sub>/HZSM-5 (300/400).

accounts for a higher percentage of transformation than benzoquinone. The products are not accumulated in the photocatalysis since benzoquinone is a good electron quencher [12] and hydroquinone a good  $\cdot\text{OH}$  quencher [13].

It can be concluded that the presence of an adsorbent like HZSM-5 zeolite immobilized in a stable polyacrylic

film significantly increases the photocatalytic activity of TiO<sub>2</sub>. Zeolite acts as a pool, increasing the concentration of the pollutant near the photocatalyst. Moreover, the presence of zeolite reduces the reaction of the reactive species formed on TiO<sub>2</sub> with the organic support. Finally, this novel combine thin film is flexible and shows good abrasion



Scheme 1. Photocatalytic activity of TiO<sub>2</sub> + acrylic film (a) and TiO<sub>2</sub> + zeolite + acrylic film (b).

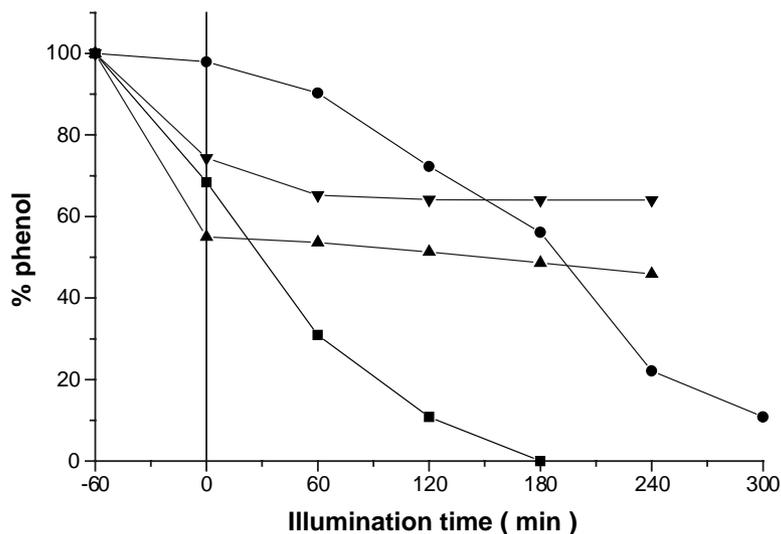


Fig. 4. Photodegradation of phenol ( $10^{-4}$  M) on different photocatalyst acrylic films. (▼) Acrylic emulsion film; (▲) HZSM-5; (●) TiO<sub>2</sub>; (■) TiO<sub>2</sub>/HZSM-5.

resistance on prolonged usage. It is an economical, practical and promising method to immobilize photocatalysts for the elimination of xenobiotic pollutants from wastewaters.

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