

Photocatalysed reaction of meso-tetraphenylporphyrin on mesoporous TiMCM-41 molecular sieves

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Abstract

A preliminary study involving 254 nm irradiation of dichloromethane suspension containing TiMCM-41 catalyst and meso-tetraphenylporphyrin (TPP) was carried out at pH 5.0. The rate of the photoreaction was considerably increased in the presence of the catalyst. Increasing the amount of the catalyst at a fixed TPP concentration enhances the rate, indicating its catalytic role in the reaction. The effect of pH, TPP concentration and calcination temperature of the catalyst on the photoreaction was also investigated. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolite and zeolite-like molecular sieves belong to a class of porous crystalline inorganic materials gaining increasing attention in heterogeneous catalysts owing to their high surface area, regular pore structure and molecular sieving properties [1]. The open framework (internal surface) structure of these materials offers a suitable heterogeneous microenvironment for a favourable manipulation of chemical and photochemical reactions [2]. One such interesting application is the zeolite-supported photocatalysis

where the zeolite serves two purposes: first, it stabilizes the active sites in a maximum dispersed state, and second, it imparts shape selectivity. As far as the photocatalysed reactions are concerned, TiO₂ supported on both microporous molecular sieve catalysts are promising [3]. Of particular attention is the significant role played by certain zeolite hosts in retarding the energy-wasting backelectron transfer reactions of photosensitisers used in solar energy research [4]. Porphyrins find their use as photosensitisers in solar energy research [5], as well as in photodynamic therapy [6]. In view of the above findings, it is of interest to investigate the photocatalytic behaviour of Ti (IV)-substituted MCM-41 (TiMCM-41) molecular sieves towards the light-induced (254 nm) photodegradation of meso-tetraphenylporphyrin (TPP).

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2. Experimental

The sample TPP (Sigma) and purified solvent dichloromethane (Qualigens) were used for all photocatalytic experiments. The pH of the solution was measured with a pH meter (Toshniwal CL46). The absorbance measurements were performed with a spectrophotometer (Hitachi U3410). The photodegradation of TPP was carried out using a well-characterized calcined TiMCM-41 catalyst [7]. A dichloromethane suspension containing fixed amount of the catalyst and a particular concentration of TPP was irradiated with 254 nm, corresponding to an absorption maximum of the catalyst. A pencil ray UV lamp (Fisher Scientific) was used as the light source. Five milliliters of the above suspension was pipetted out after different intervals of irradiation, centrifuged, then the absorbance of TPP at 445 nm (λ_{\max} of TPP) was measured spectrophotometrically. Progress of the reaction was monitored based on the absorbance measurements at different time intervals of irradiation. The photoprocess was found to follow a first order kinetics, evidenced by linear (first order) plot of $\log(\text{Abs})_{445}$ vs. time and the rate constant (k) was determined from the slopes. The rate of the photoreaction was obtained by the multiplication of k with the corresponding TPP concentration, viz., $k[\text{TPP}]$.

3. Results and discussion

3.1. Effect of catalyst concentration

The rate of heterogeneous photoprocess was measured with varying amounts of the catalyst in the presence of oxygen at a fixed [TPP] (0.5×10^{-5} M), pH (5.0) in 40 ml of dichloromethane. It was observed that the rate increased with the increase in the amount of catalyst (Fig. 1), indicating the photodegradation of TPP. Fig. 2 shows the variation of [TPP] absorbance at different time intervals with respect to various catalyst amounts. It is therefore

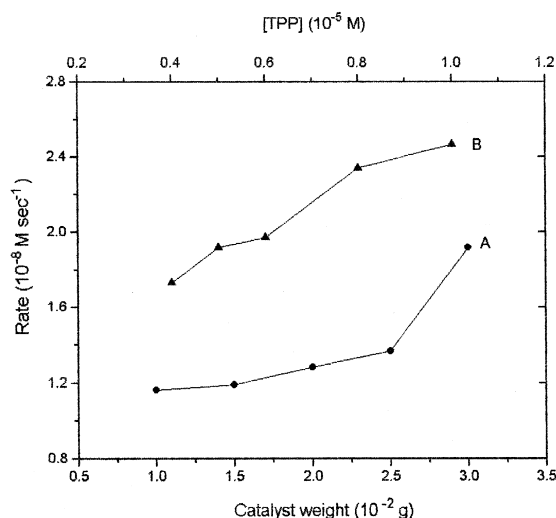


Fig. 1. The effect of catalyst weight (A) and TPP concentration (B) on the reaction rate.

clear from the figure that the photodegradation of TPP occurs linearly with time for each of the catalyst concentration. In a separate experiment, it was ensured that in the absence of catalyst, the rate of the photoreaction of TPP (at 254 nm irradiation) was negligible. The observed increase in the photoreaction of TPP in the presence of the catalyst suggests that the irradiation (at 254 nm) leads to a photooxidation (\equiv photoionisation) of TPP to give $\text{TPP}^{+\cdot}$, which is facilitated due to the electron-accepting ability (influence) of TiMCM-41 [8,9]. In fact, the electron-accepting behaviour of irradiated TiMCM-41 has also been demonstrated in a study involving the photocatalytic reduction of CO_2 with H_2O yielding CH_3OH [10].

3.2. Effect of TPP concentration

At a fixed amount of the catalyst (0.03 g) and solvent (40 ml), with a pH of 5.0, the rate of the photoreaction was measured with various initial [TPP]. It was observed that the reaction rate increased linearly with [TPP] (see Fig. 1).

The variation of TPP degradation with respect to different [TPP] at different time intervals is shown in Fig. 3. The linear plots in Fig.

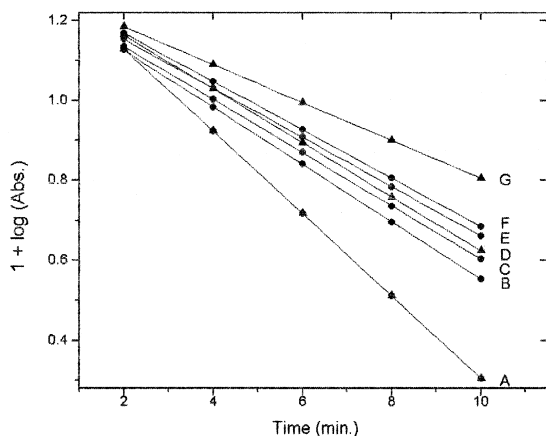


Fig. 2. The effect of the variation of catalyst weight (●) [0.5×10^{-5} M TPP/40 ml; pH 5.0) (A, B, C, E, F are 1.0, 1.5, 2.0, 2.5, and 3.0×10^{-2} g TiMCM-41, respectively)] and the influence of pH (▲) [0.5×10^{-5} M TPP/40 ml; 3.0×10^{-2} g TiMCM-41) (A, D and G are pH 5, 7 and 9, respectively)] on the TPP concentration.

3 indicate that the reaction follows a first order kinetic behaviour.

3.3. Effect of pH

The effect of pH on the photoreaction was investigated using a TPP of 0.5×10^{-5} M and a catalyst (0.03 g) in the presence of a 40-ml dichloromethane solvent. A decrease in the reaction rate with an increase in pH from 5.0 to

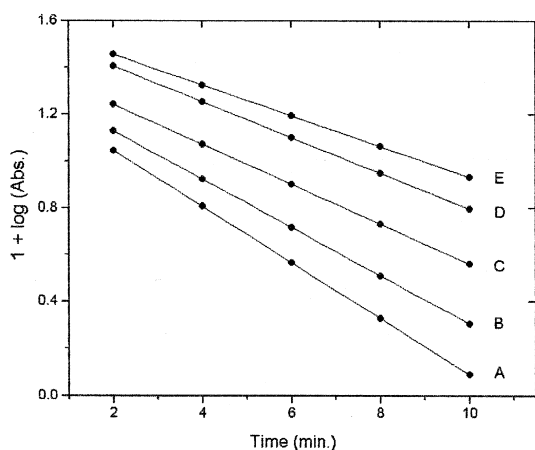


Fig. 3. The effect of the variation of TPP concentration (3.0×10^{-2} g TiMCM-41/40 ml; pH 5.0) (A, B, C, D, E are $0.4, 0.5, 0.6, 0.8,$ and 1.0×10^{-5} M [TPP], respectively).

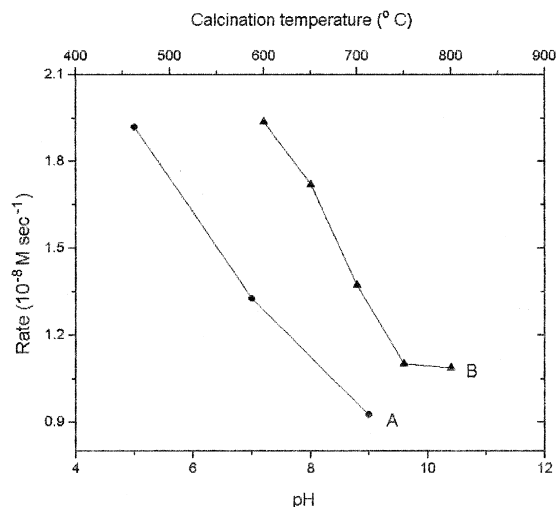


Fig. 4. Influence of pH (A) and calcination temperature (B) on the reaction rate.

9.0 were observed (Fig. 4). It is well-known that porphyrins can also undergo photoreduction. The higher reactivity of the photoreaction at acidic pH shows the preferred tendency of TPP to get reduced in acidic solution [11]. Moreover, the photodegradation of TPP with respect to pH at different time intervals is shown in Fig. 2. The linearity of each line (at each pH) shows that the reaction obeys first order kinetics at each pH.

3.4. Effect of calcination temperature

The effect of the calcining temperature (2 h at each temperature) on the photoreaction rate is shown in Fig. 4. The rate of photoreaction decreases as the calcination temperature of catalyst increases. It is, however, understandable that the increase of calcination temperature may dislodge titanium from the framework, and hence, retard the photoreaction.

4. Conclusion

In summary, it may be deduced that TiMCM-41 catalyst is active towards the photodegradation of TPP. Undoubtedly, the mesoporous ma-

trix provides a better dispersion of active titanium sites and freely accesses the TPP molecules to these isolated sites, thereby facilitating the photocatalytic activity. The present work, however, may serve as a preliminary step towards designing further studies on the photodynamic behaviour of the porphyrins in constrained environment.

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