

Heteropolytungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$)—encapsulated into the titanium-exchanged HY (TiHY) zeolite: a novel photocatalyst for photoreduction of methyl orange

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Abstract

The preparation, characterization and photoreactivity of heteropolytungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$)—encapsulated into the titanium-exchanged HY (TiHY) zeolite is presented. In the photoreaction study of methyl orange in the presence of HPA-encapsulated TiO_2 zeolite, a 20-fold increase in the photoreaction rate is observed as compared to the rate observed in the presence of HPA-encapsulated HY zeolite without TiO_2 .

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1. Introduction

In the recent years, solid heteropolyacids (HPA) are known to be active reuse catalysts for a variety of homogeneous and heterogeneous acid catalyzed reactions due to their strong Bronsted acidity character compared to homogeneous catalysts such as H_2SO_4 , HCl , AlCl_3 , etc. [1,2]. For reuse of the HPA catalysts many researchers prefer to support HPA on solid surfaces like carbon, SiO_2 , Y-type, MCM-41 zeolites, etc. in order to make thermally stable immobilized catalyst [3–5].

Thus prepared immobilized catalysts could exhibit high catalytic activity for the conversion of formation of large organic molecules. Among the immobilized catalysts, important novel catalytic properties were ob-

served when HPA were either deposited at the surface of the zeolite or encapsulated in its pores [6–9]. This is because zeolites have unique uniform pores and channel sizes (3–8 Å) which provide selective exclusion of molecules or ions. Zeolites may also be used as constrained systems for the preparation of semiconductors (TiO_2) with limited particle size and shape, and they can provide with specific photophysical properties such as the control of charge transfer and electron transfer processes [10–13]. So our main intention is compiling both the above properties in order to prepare novel photocatalyst.

In this work, we have studied the preparation of the HPA encapsulated into TiHY zeolite with the aim to observe the photoinduced interfacial electron transfer from the titanium in TiHY zeolite to the encapsulated HPA, which induces the synergistic enhancement of the catalytic activity of photoreduction of methyl orange (MeOr) analogous to the plant photosystem.

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2. Experimental

2.1. Materials and methods

The chemicals used are NaY zeolite, ammonium titanyl oxalate monohydrate, sodium tungstate (Aldrich) and methyl orange (Fluka). All the other chemicals used were purest research grade available. Diffused reflectance UV-Vis spectra of the samples were recorded using a Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere. IR spectra are recorded with a JASCO FT/IR 410 spectrophotometer by employing KBr pellet technique. ^{31}P NMR MAS spectra of 161.921 MHz were recorded at room temperature on a Bruker (DSX 400) spectrometer using H_3PO_4 as external reference. For the photoreduction processes, Xe arc lamp ($\lambda \geq 320$ nm) was used as a light source. Progress of the reaction was monitored spectrophotometrically using a SINCO UVS 2040 spectrophotometer after a certain period of irradiation of the sus-

pension and then filtered with a $0.45\ \mu\text{m}$ PVDF filter.

2.2. Preparation of the photocatalyst

HY zeolite [6] were prepared from NaY zeolite ($\text{Si}/\text{Al} = 2.47$) by ion exchange with a 10 wt.% NH_4Cl solution. The TiHY zeolite (7.2 Ti species in each unit cell) is prepared via ion exchange of HY zeolite (1 g) with an aqueous solution of ammonium titanyl oxalate monohydrate (5.28×10^{-2} mol/l) [12]. In order to avoid basicity of aluminium, which accelerates the decomposition of HPA, Y-type zeolite was dealuminated in a steam atmosphere for 10 h before the TiHY zeolite preparation.

Encapsulation of HPA in the titanium-exchanged HY zeolite matrix was carried out by an in situ synthesis of this compound in a similar manner to Bailar [14] procedure for the synthesis of HPA (i.e. the ratio of sodium tungstate and disodium phosphate 1:1/12). The preparation procedure is as follows: 2 g of TiHY

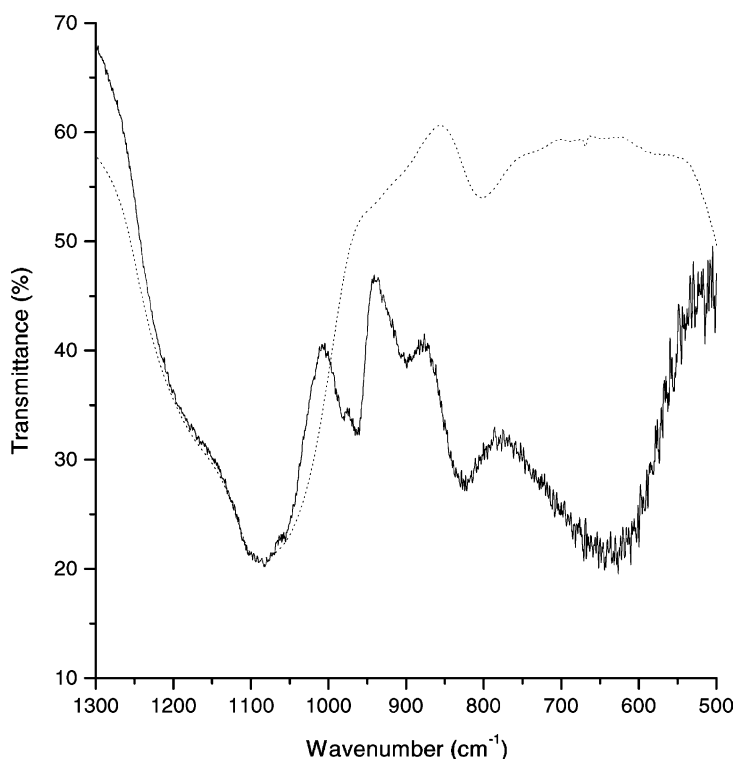


Fig. 1. IR spectra of TiHy zeolite (···) and HPA-encapsulated into TiHY zeolite (—).

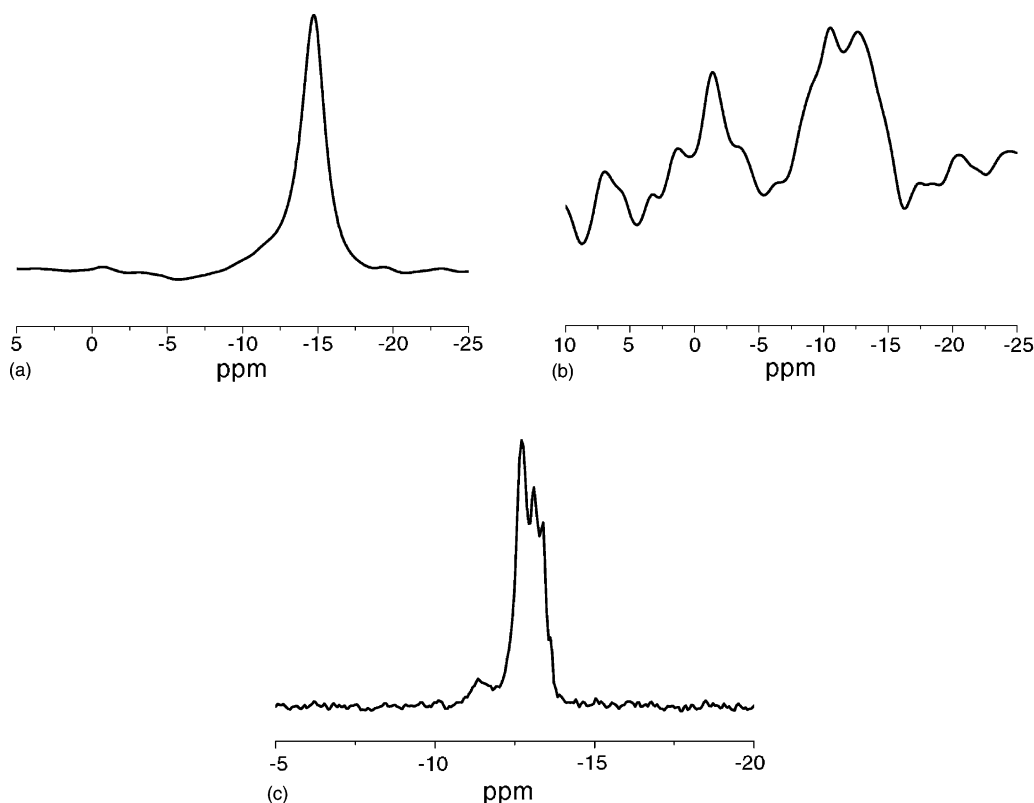


Fig. 2. ^{31}P MAS NMR spectra of: (a) HPA; (b) HPA encapsulated into HY zeolite; (c) HPA encapsulated into TiHY zeolite.

zeolite was added to a solution of disodium phosphate [$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; 0.5195 g] in water and the whole mixture was stirred to 2 h at ambient temperature. Then a solution of sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$; 14.693 g) was added dropwise to the suspension. After 1.5 h of stirring, a stoichiometric amount of HCl was added dropwise. The suspension was stirred further for 4 h. Finally, the zeolite was separated from liquid and washed thoroughly with hot doubly distilled water.

3. Results and discussion

3.1. Characterization of the photocatalyst

Infrared analysis of the encapsulated heteropolyacids confirmed the presence of the fingerprint bands below 1100 cm^{-1} which are characteristic of

the $\text{PW}_{12}\text{O}_{40}^{3-}$ ion, i.e. the Keggin unit. IR spectra recorded for the encapsulated HPA into TiHY zeolite shows absorption bands at 1083, 965, 899 and 821 cm^{-1} , which are typical of Keggin unit as well as the titanium-exchanged HY zeolite (Fig. 1). The peak at 1083 cm^{-1} are assigned to M–O stretchings (where M = P/Ti) and the peak at 965 cm^{-1} may be M=O stretching (where M = W). The other two peaks (899 and 821 cm^{-1}) may be due to M–O–M vibrations (where M = Si, Al, W). The fact that all the peaks are found to be overlapped over the other leads to conclude that both the exchanged titanium and the encapsulated Keggin unit are present in the zeolite cavity [8,9,11,13].

Further, in order to confirm the prepared novel photocatalyst we adopt NMR for all the prepared samples. In Fig. 2, ^{31}P NMR MAS spectra of the sample are shown. Pure crystals of the heteropolytungstate gave a sharp peak at -14.799 ppm whereas the encapsu-

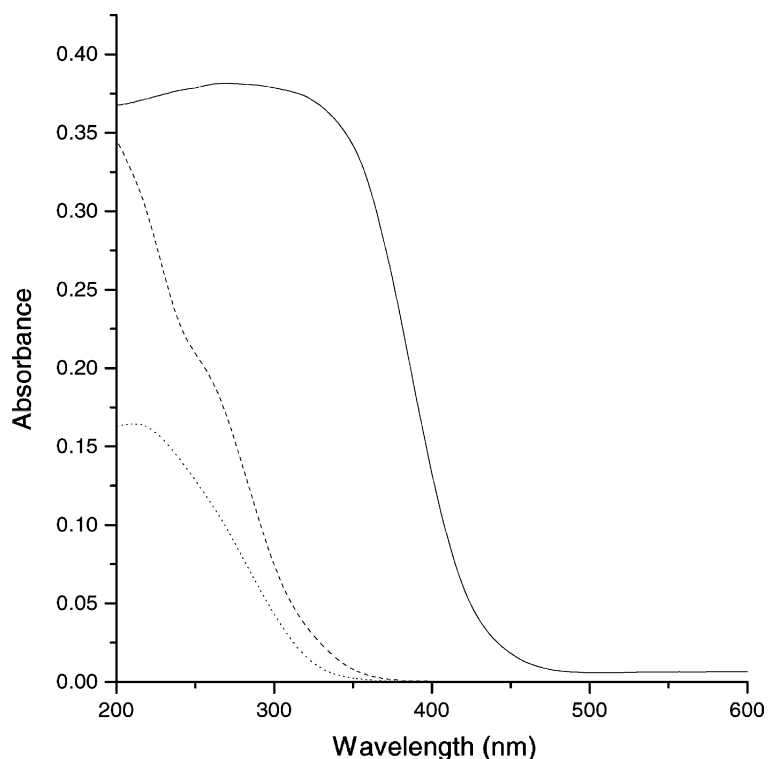


Fig. 3. UV-Vis diffused reflectance spectra of: (—) HPA encapsulated into TiHY zeolite; (---) HPA encapsulated into HY zeolite; (···) TiHY zeolite.

lated HPA into HY zeolite shows broad peaks from -10.52 to -14.6 ppm. Five peaks (-11.36 , -12.72 , -13.09 , -13.37 and -13.59 ppm) were observed for the HPA-encapsulated TiHY zeolite, suggesting that the Keggin unit is present in the zeolite cavity. Such broad peaks may be due to the distortion of isotropic chemical shifts of ^{31}P due to various electronic environments of HPA adsorbed in the mesoporous of the zeolite and also due to the various number of water molecules in the proximity of the polyanion [8,9,15–17].

Fig. 3 shows the diffused reflectance spectra of HPA encapsulated into TiHY zeolite, which is different from that of the titanium-exchanged HY (TiHY) zeolite and HPA-encapsulated HY zeolite [11]. The absorption for the HPA-encapsulated TiHy zeolite is further red shifted (400 nm), which is vitally important for the photoinduced electron transfer processes.

3.2. Photoreduction of methyl orange (MeOr)

The rate of heterogeneous photoprocess was measured with varying amount of the catalyst at a fixed [MeOr] (5×10^{-5} M), pH (4.0) in 30 ml of ethanol. It was observed that the rate increased with the increase in the amount of catalyst, indicating the photodegradation of [MeOr]. Fig. 4 shows the variation of MeOr absorbance at different time intervals with respect to various catalyst amounts. It is therefore clear from the figure that the photodegradation of MeOr occurs linearly with time for each of the catalyst concentration. In a separate experiment, it was confirmed that in the absence of photocatalyst, the rate of the photoreaction of MeOr was negligible. The observed increase in the photoreaction of MeOr in the presence of the catalyst suggests that the irradiation leads to a photoreduction of MeOr to hydrazine (Hz) [18,19].

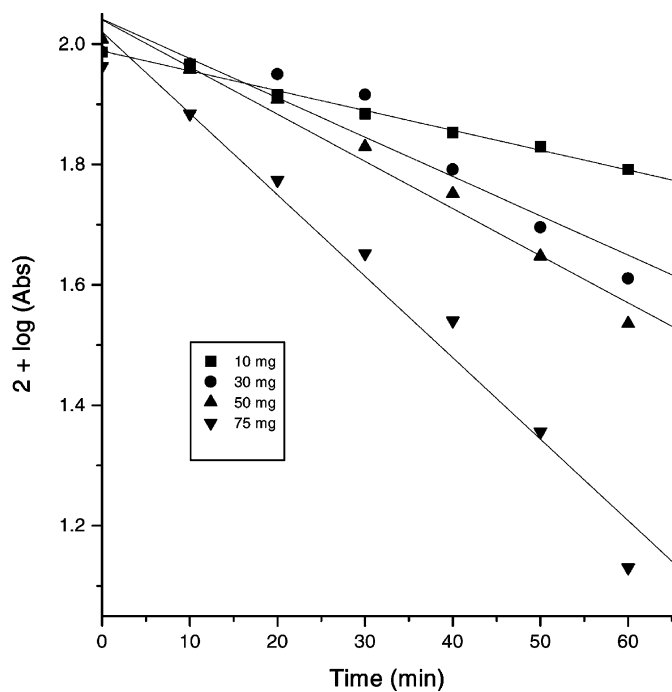
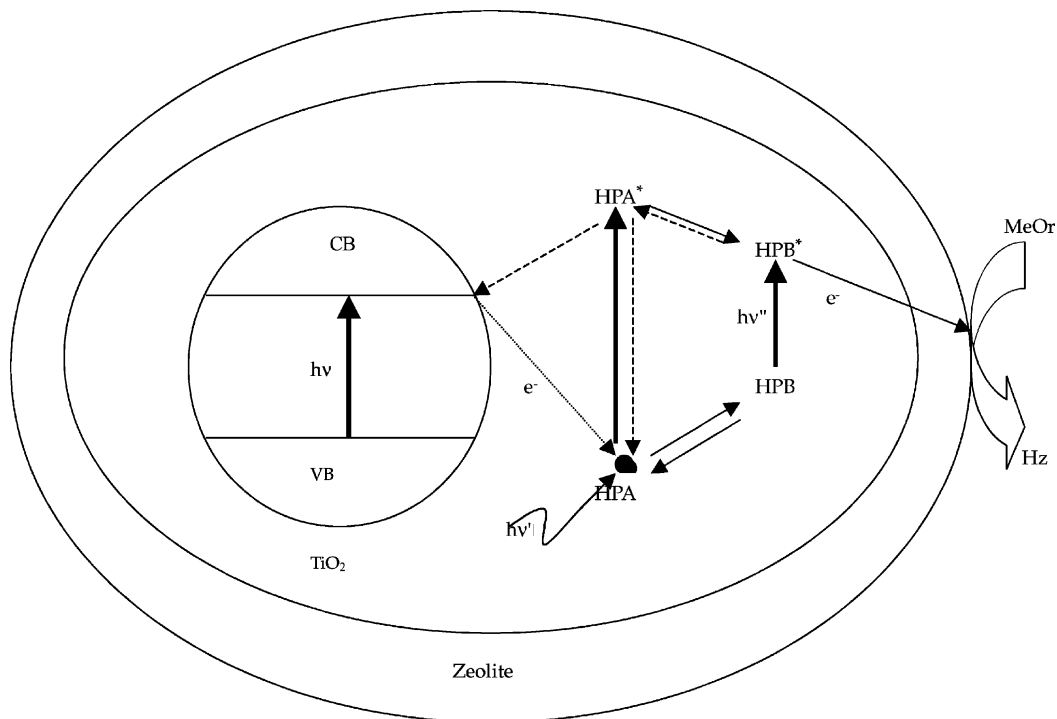


Fig. 4. Plot of variation of catalyst (HPA-TiHY zeolite) upon irradiation time in the presence of fixed initial concentration of MeOr (5×10^{-5} M).



Scheme 1. The proposed mechanism for photoreduction of methyl orange by using the HPA encapsulated into TiHY zeolite.

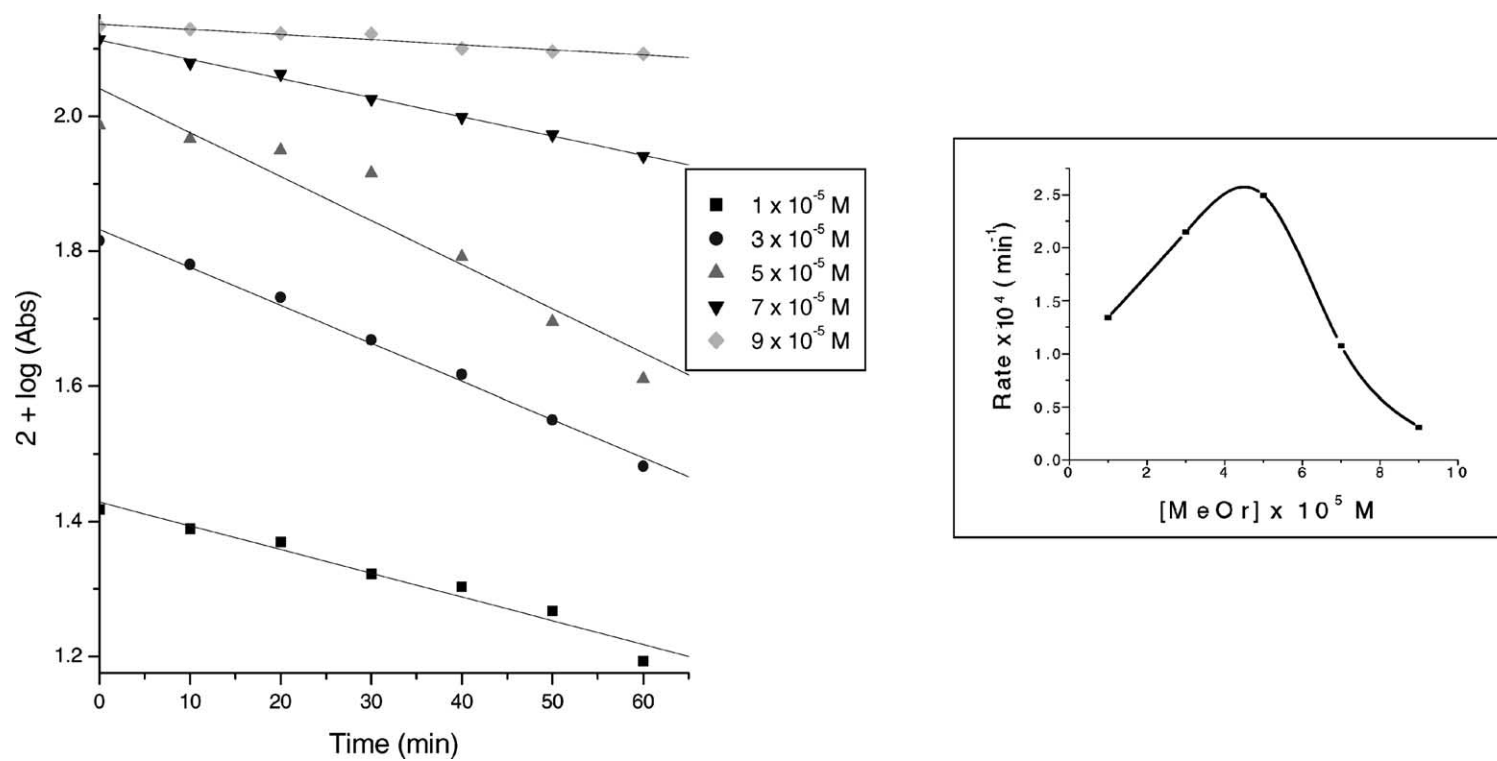


Fig. 5. Plot of variation of concentration of MeOr upon irradiation time in the presence of a fixed amount of HPA–TiHY zeolite (30 mg). Inset shows plot of photoreduction rate of MeOr vs. the concentration of MeOr in the presence of fixed HPA-encapsulated TiHY zeolite (30 mg).

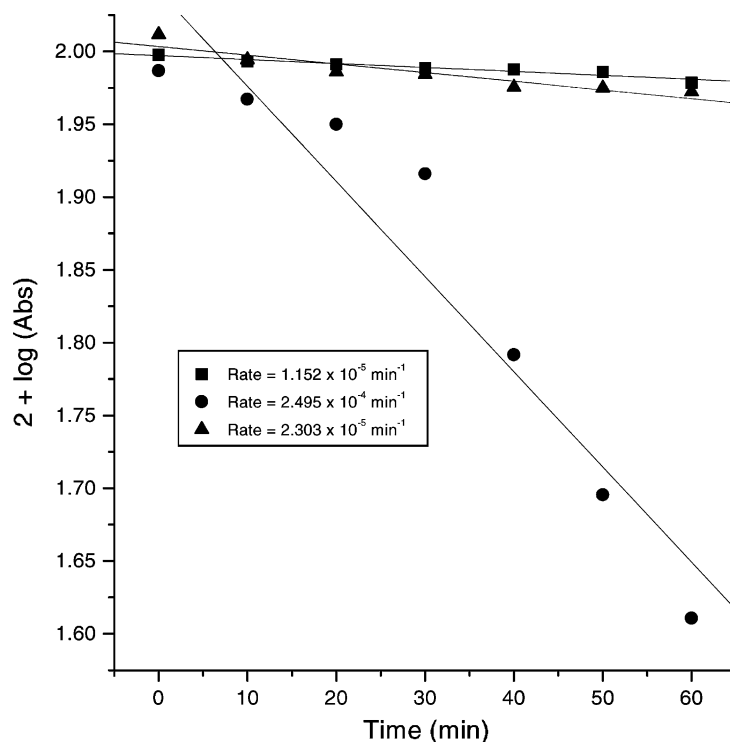


Fig. 6. Comparison of photoreduction rate of MeOr in the presence of: HPA-encapsulated HY zeolite (■); HPA-encapsulated TiHY zeolite (●) and TiHY zeolite (▲). Concentration of both catalyst and [MeOr] is the same (30 mg, 5×10^{-5} M).

At a fixed amount of the catalyst, the rate of the reaction was measured with the various initial concentration of MeOr. It was observed that the reaction rate increased with increasing concentration to 5×10^{-5} M and then decreases very rapidly (inset of Fig. 5). This may be due to saturation of adsorption of MeOr over the catalyst surface. The variation of MeOr degradation with respect to different [MeOr] at different time intervals is shown in Fig. 5. The linear plots in Fig. 5 indicate that the reaction follows first order kinetic behaviour.

3.3. Comparison of photocatalytic efficiency

The observed rate of reaction on the HPA encapsulated into TiHY zeolite is found to be 20 times as high as that on the HPA encapsulated into HY zeolite and 9 times as high as that on TiHY zeolite without encapsulated HPA (Fig. 6). Similarly a four-fold increase in the rate is observed when compared to the HPA–TiO₂

colloidal system. Thus, in the prepared HPA encapsulated into TiHY zeolite the photoinduced interfacial electron transfer should take place from the titanium in HY zeolite to the encapsulated HPA, followed by the synergistic enhancement of the catalytic activity of photoreduction of MeOr in a way analogous to the plant photosystem (Scheme 1) as proposed previously for the colloidal system [19].

4. Conclusion

The HPA encapsulated into TiHY zeolite is very active as a photocatalyst towards the photoreduction of methyl orange. Undoubtedly, the zeolite matrix provides a better dispersion of active titanium sites and free accesses of the MeOr 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

photophysical and photochemical aspect, being under scrutiny in our laboratory at present.

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References

- [1] N. Mizuno, M. Misono, *J. Mol. Catal.* 86 (1994) 319.
- [2] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, *J. Mol. Catal.* 74 (1992) 247.
- [3] Y. Izumi, K. Urabe, *Chem. Lett.* (1981) 663.
- [4] V.M. Mastikhin, S.M. Kulikov, A.V. Nosov, I.V. Kozhevnikov, I.L. Mudrakovsky, M.N. Timofeeva, *J. Mol. Catal.* 60 (1990) 65.
- [5] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. Van Bekkum, *J. Mol. Catal.* 114 (1996) 287.
- [6] S.R. Mukai, T. Masuda, I. Ogino, K. Hashimoto, *Appl. Catal. A Gen.* 165 (1997) 219.
- [7] S.R. Mukai, L. Lin, T. Masuda, K. Hashimoto, *Chem. Eng. Sci.* 56 (2001) 799.
- [8] K. Pamin, A. Kubacka, Z. Olejniczak, J. Haber, B. Sulikowski, *Appl. Catal. A Gen.* 194 (2000) 137.
- [9] B. Sulikowski, J. Haber, A. Kubacka, K. Pamin, Z. Olejniczak, J. Ptaszynski, *Catal. Lett.* 39 (1996) 27.
- [10] H. Chen, A. Matsumoto, N. Nishimiya, K. Tsutsumi, *Colloids Surf.* 157 (1999) 295.
- [11] X. Liu, K. Kong Iu, J. Kerry Thomas, *Chem. Phys. Lett.* 195 (1992) 163.
- [12] X. Liu, K. Kong Iu, J. Kerry Thomas, *J. Chem. Soc. Faraday Trans.* 89 (1993) 1861.
- [13] Y. Kim, M. Yoon, *J. Mol. Catal. A: Chem.* 168 (2000) 257.
- [14] J.C. Bailar, Jr., H.S. Booth (Ed.), *Inorganic Synthesis*, vol. 1, McGraw-Hill, New York, 1939, p. 132.
- [15] D.K. Lyon, W.K. Miller, T. Novet, P.J. Domaille, E. Evitt, D.C. Johnson, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7209.
- [16] S. Uchida, K. Inumaru, J.M. Dereppe, M. Misono, *Chem. Lett.* (1998) 643.
- [17] Y. Kanda, K.Y. Lee, S.I. Nakata, S. Asaoka, M. Misono, *Chem. Lett.* (1988) 139.
- [18] G.T. Brown, J.R. Darwent, *J. Chem. Soc. Faraday Trans. I* 80 (1984) 1631.
- [19] M. Yoon, J.A. Chang, Y. Kim, J.R. Choi, K. Kim, S.J. Lee, *J. Phys. Chem. B* 105 (2001) 2539.