

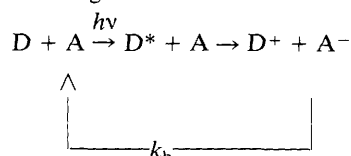
Separation of Photogenerated Redox Species in Zeolites *via* Ion-exchange

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The ion-exchange properties of the zeolite are exploited to remove $MV^{+\cdot}$ formed upon photolysis of zeolite Y containing encapsulated $Ru(bpy)_3^{2+}$ and MV^{2+} , thereby allowing ready access to the photogenerated product.

Storage as well as conversion of solar energy to other useful forms of energy is an active area of research.¹ Light-induced electron-transfer reactions provide an attractive route for the conversion of solar to chemical energy.² For example, a photoexcited donor D can interact with an acceptor molecule A as shown below to generate D^+ and A^- .



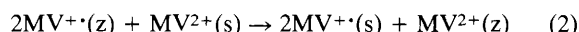
There are several problems that need to be solved in designing chemical systems that can successfully accomplish this goal. These include avoiding the back-reaction (k_b) of D^+ and A^- to regenerate D and A, which dissipates the light energy into useless thermal energy. If the back-reaction can be avoided, it will then be necessary to retrieve the chemical potential stored in the photoproducts, with subsequent regeneration of D and A. This will need access to the charge separated redox pairs.

It has been recognized that if D^+ and A^- can be spatially separated after charge transfer, the back electron-transfer reaction can be retarded, as is evident in photosynthesis.³ Photochemistry on various microheterogeneous systems have been examined to accomplish this goal.² Examples include silica,⁴ sol-gel glasses,⁵ layered compounds,⁶ polyelectrolytes,⁷ micelles⁸ and cyclodextrins⁹ with varying degrees of success, resulting in charge separation that lasts for microseconds to hours. The novel cage architecture of microporous aluminosilicate zeolites has been exploited in various photochemical studies.¹⁰ The reaction between photoexcited $Ru(bpy)_3^{2+}$ as donor and methylviologen (MV^{2+}) as acceptor with both species inside zeolites is the subject of this study. A novel arrangement is possible in the cage network of zeolite Y, since the 12 Å $Ru(bpy)_3^{2+}$ can be trapped within the 13 Å supercage,¹¹ yet can readily interact with MV^{2+} in neighbouring supercages through the 7 Å windows.^{12,13} The intrazeolitic oxidative quenching of $Ru(bpy)_3^{2+*}$ by MV^{2+} occurs readily.¹³ Though a rapid back reaction (half-life *ca.* 10–20 μs) does occur between the $Ru(bpy)_3^{2+}$ and $MV^{+\cdot}$, the zeolite architecture provides an alternate channel by which the electron on the $MV^{+\cdot}$ hops on to other viologens in neighbouring supercages, resulting in charge separation that lasts for tens of minutes.¹³

In this communication, we address the issue of accessing the charge-separated species during photolysis, in particular, the $MV^{+\cdot}$, by exploiting the ion-exchange properties of the zeolite. This results in removal of the photolytically generated $MV^{+\cdot}$ from the zeolite into the surrounding solution, thus allowing separation of photogenerated charges as well as unhindered access to the reduced equivalent. In a previous study, we have shown that interfacial electron transfer across the zeolite-solution interface can also accomplish this task.¹⁴

During the photolysis of the $Ru(bpy)_3^{2+}$ - MV^{2+} zeolite in the solid state,^{12,13} the photolytic reaction of interest is shown in eqn. (1) where z denotes intrazeolitic species. The loading $Ru(bpy)_3^{2+*}(z) + MV^{2+}(z) \rightarrow Ru(bpy)_3^{3+}(z) + MV^{+\cdot}(z)$ (1) of MV^{2+} needs to be *ca.* 2 molecules per supercage for optimum generation of the $MV^{+\cdot}$ radical¹³ and the radical

formation occurs over a time period of tens of minutes. In this study, we examine the possibility of removing the $MV^{+\cdot}(z)$ into solution *via* the following ion-exchange reaction during photolysis, shown in eqn. (2), s denoting the solution surrounding the zeolite.



It is necessary to know the equilibrium constant and kinetics of reaction (2), in order to determine the feasibility of removal of the $MV^{+\cdot}$ from the zeolite into solution. This is dependent on intrazeolitic diffusion coefficients and the concentrations of MV^{2+} and $MV^{+\cdot}$. Considering that the dimensions of MV^{2+} are $12.6 \times 6.4 \times 3.8$ Å¹⁵ and that it has to negotiate its passage through 7 Å windows, it can be expected that the success of reaction (2) for charge separation may be limited by the diffusion process. There is only limited information about the kinetics of the ion-exchange of cations in zeolites,¹⁶ and large cations, in particular. From this available information, it is difficult to determine the feasibility of using reaction (2). Since chemical preparation of $MV^{+\cdot}$ exchanged zeolite Y necessitates the presence of other interfering ions in solution, direct information about its rate of ion-exchange cannot be obtained. A measure of the kinetic efficiency could be obtained by examining zeolites containing ions similar in size to $MV^{+\cdot}$. We chose $Co(C_5H_5)_2^+$ exchanged zeolite Y for that purpose, since the dimensions of the $Co(C_5H_5)_2^+$ ion are 6.8×5.6 Å,¹⁷ and its diffusion coefficient has been reported to be similar to that of MV^{2+} .¹⁸ Its appearance in solution upon ion-exchange from the zeolite is also readily monitored by the electronic band at 405 nm.¹⁹ Fig. 1 shows the ion-exchange of $Co(C_5H_5)_2^+$ -zeolite Y with a 0.1 mol dm⁻³ solution of MV^{2+} . It is clear that the ion-exchange process reaches equilibrium within the time period of photolysis (tens of minutes) and supports the use of reaction (2) for separating the photoproducts.

Previous photolysis studies^{12,13} were carried out in the solid state. In order to exploit the ion-exchange process, the photolysis needs to be carried out in the presence of MV^{2+} in solution. Two factors need to be taken into consideration in deciding upon the MV^{2+} concentration. These include the

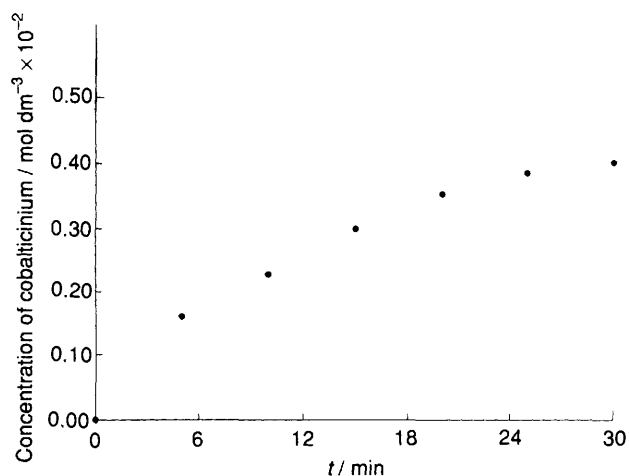


Fig. 1 Measure of the release of $Co(C_5H_5)_2^+$ from zeolite Y upon ion-exchange with 0.1 mol dm⁻³ MV^{2+} as a function of time

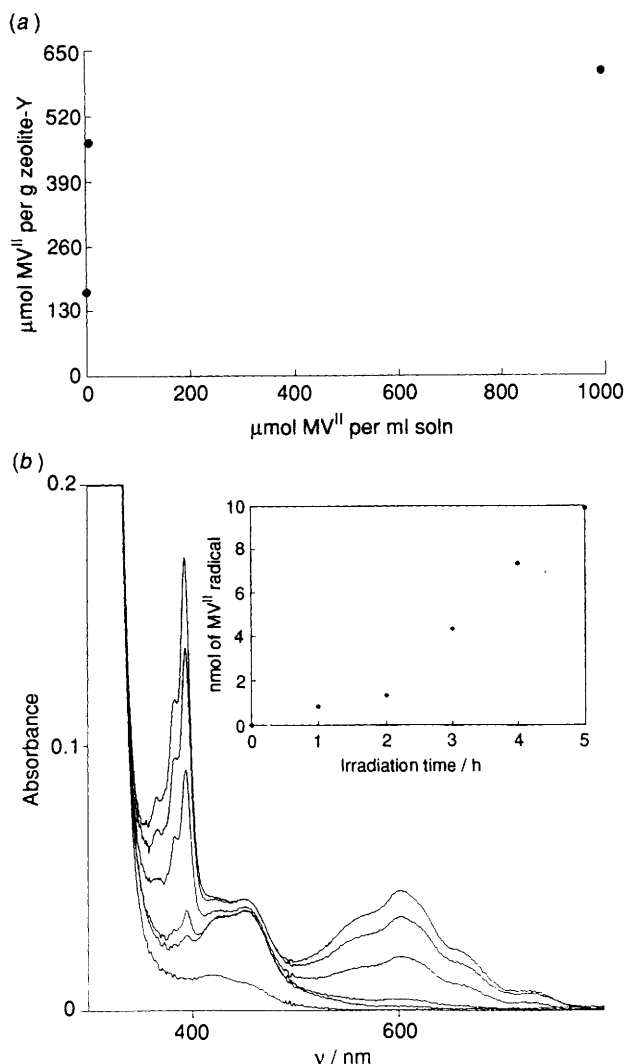


Fig. 2 (a) Isotherm for ion-exchange of NaY with MV^{2+} . (b) Electronic spectra of MV^{2+} in solution as a function of photolysis time. Inset: Plot of the growth of $[MV^{2+}]$ as a function of time.

appropriate loading level of the MV^{2+} in the zeolite as well as the MV^{2+} concentration in the surrounding solution. In order to decide on these factors, the isotherms for MV^{2+} exchange with Na-Y were examined. Fig. 2(a) shows the isotherm data. At maximum exchange, the MV^{2+} concentration reaches about ca. 1.3 molecules per supercage. The previous solid-state studies,^{12,13} indicated that it is necessary to keep the intrazeolitic loading high. Thus, a 0.1 mol dm^{-3} MV^{2+} solution, that leads to the saturation loading of MV^{2+} in the zeolite and yet provides enough MV^{2+} in solution was chosen as the optimum concentration for the photolysis studies.

The photolysis was carried out in an anaerobic environment, with a $Ru(bpy)_3^{2+}$ -zeolite Y [1 molecule $Ru(bpy)_3^{2+}$ per 10 supercages] pellet (ca. 1 cm) immersed in a 0.1 mol dm^{-3} solution of MV^{2+} .[†] The zeolite was photolysed with 420–680

nm (200 mW) radiation, and the supernatant solution was monitored via UV-VIS spectroscopy for MV^{2+} . Fig. 2(b) shows the solution spectra as a function of photolysis time. The characteristic absorption spectrum of MV^{2+} (395, 602 nm) is observed to grow in with photolysis. In order for these experiments to be successful, it is essential to deoxygenate the samples extensively, since the MV^{2+} is generated in small amounts and is readily oxidized with O_2 .[†] The inset of Fig. 2(b) shows the growth of MV^{2+} plotted as a function of photolysis time. The kinetics is complicated by the rate of photolytic MV^{2+} generation as well as the rate of ion-exchange. After 4 h of photolysis, the yield of MV^{2+} in solution is about 0.3% of the total $Ru(bpy)_3^{2+}$ in the zeolite. However, since the radiation only penetrates a small, yet undetermined fraction of the pellet, the conversion relative to $Ru(bpy)_3^{2+}$ content is significantly higher. Methods to measure the photochemical efficiency of this process are being developed. Once the MV^{2+} is separated from the zeolite into solution, its potential utility can be readily exploited.

In summary, this communication shows that the ion-exchange properties of the zeolites offers a strategy for removing MV^{2+} from the zeolite into solution during photolysis. Compared to other microheterogeneous supports that have been used for photochemical charge separation, this feature of the zeolite presents a simple method for access to the photogenerated product.

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[†] To observe the radical MV^{2+} , it is necessary to deoxygenate samples thoroughly. This was done by degassing the $Ru(bpy)_3^{2+}$ -Y at 10^{-4} Torr (1 Torr = 133.322 Pa) for 12 h. Freeze-pump cycles were done on the 0.1 mol dm^{-3} MV^{2+} solution three times and mixed with the zeolite sample in an anaerobic glove box in an anaerobic UV-VIS cell.