Photoinduced charge-separation using 10-methylacridinium ion loaded in zeolite Y as a photocatalyst with negligible back electron transfer across the zeolite–solution interface

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Photoinduced electron transfer from Fe^{2+} loaded in zeolite Y to the singlet excited state of 10-methylacridinium ion in the zeolite occurs to give the acridinyl radical which reduces 7,7,8,8-tetracyanoquinodimethane in acetonitrile solution to yield the radical anion; the back electron transfer from the radical anion to Fe^{3+} across the zeolite–solution interface is shown to be negligibly slow.

Considerable efforts have so far been devoted to develop photocatalytic systems in which a back electron transfer following the initial photoinduced electron transfer can be retarded to achieve long-lived charge separation.[1–7] The most remarkable result has recently been reported by Dutta *et al.*[8,9] by encapsulation of $Ru(bpy)_3{}^{2+}$ in the supercage of zeolite Y to retard the back electron transfer across the zeolite–solution interface. In fact, the radical anion of propylviologen sulfonate (PVS) formed by photoinduced electron transfer from $Ru(bpy)_3{}^{2+}$ in the zeolite to PVS in solution persisted for hours.[8] However, the absence of back electron transfer across the zeolite–solution interface has not been established experimentally. Moreover, it should be resolved as to why the back electron transfer between stable ground state molecules, which is thermodynamically a much more favoured process than the forward electron transfer, does not occur appreciably within hours although the forward electron transfer from the short-lived excited state of $Ru(bpy)_3{}^{2+}$ to PVS occurs across the zeolite–solution interface within microseconds.

We report herein a photocatalytic system that achieves complete charge separation between Fe^{3+} in zeolite Y and an acceptor radical anion in solution by using 10-methylacridinium ion ($AcrH^+$) loaded in the zeolite as a photocatalyst. The absence of the back electron transfer across the zeolite–solution interface has been confirmed experimentally.

Both Fe^{2+} (1.9×10^{-5}–8.2×10^{-5} mol g^{-1}, 0.38–1.3 molecules per 10 supercages) and $AcrH^+$ (1.4×10^{-4} mol g^{-1}, 2.7 molecules per 10 supercages) were loaded into Na-Y zeolite by ion exchange with $Fe(ClO_4)_2$ and $(AcrH)ClO_4$ in acetonitrile (MeCN).† The visible absorption band of $AcrH^+$ incorporated in the zeolite was observed at λ_{max} = 362 nm, which is significantly red-shifted compared with that in an MeCN solution (λ_{max} = 358 nm).[10] Photolysis of the ion-exchanged zeolite (20 mg) suspended in an MeCN solution of TCNQ (1.0×10^{-3} mol dm^{-3}) under irradiation of a mercury lamp through a Pyrex filter at 298 K leads to the appearance of $TCNQ^{\cdot -}$ (λ_{max} 842 nm, ε_{max} 4.33×10^4 dm^3 mol^{-1} cm^{-1})[11] in solution. The absorption spectra of the suspended solution stirred with a magnetic stirrer were monitored using an integrating sphere attachment. The concentration of $TCNQ^{\cdot -}$ after photolysis for 21 h was determined as 5.5×10^{-5} mol dm^{-3}, which corresponds to 13% of the initial amount of Fe^{2+} loaded in the zeolite. The initial rate of formation of $TCNQ^{\cdot -}$ under irradiation of the mercury lamp increases with an increase in the amount of Fe^{2+} loaded in the zeolite, $[Fe^{2+}]$, to reach a limiting value at higher concentrations as shown in Fig. 1. A standard actinometer (potassium ferrioxalate)[12] was used for the quantum yield (Φ) determination. The Φ value for the formation of $TCNQ^{\cdot -}$ in the photolysis of the Fe^{2+}–$AcrH^+$–zeolite sample (10 mg, Fe^{2+} = 8.2×10^{-5} mol g^{-1}) suspended in MeCN containing TCNQ (1.0×10^{-4} mol dm^{-3}) over a period of 40 min was estimated as 5.1×10^{-4}, which is compatible with the Φ value reported for the $Ru(bpy)_3{}^{2+}$–zeolite system.[8]

Irradiation of the absorption band of $AcrH^+$ (362 nm) of the Fe^{2+}–$AcrH^+$–zeolite suspended in MeCN causes fluorescence as shown in Fig 2. The fluorescence intensity (I) decreases with an increase in $[Fe^{2+}]$. The fluorescence decay obeyed the first-order kinetics. The fluorescence lifetime (τ) also decreases with an increase in $[Fe^{2+}]$. From the Stern–Volmer plot of I_0/I and τ_0/τ *vs.* $[Fe^{2+}]$ are obtained the quenching constant K_q as 2.5×10^4 g mol^{-1}.

The formation of Fe^{3+} inside the zeolite accompanied by the formation of $TCNQ^{\cdot -}$ in solution was confirmed by the EPR spectra. The EPR spectra of the Fe^{2+}–$AcrH^+$–zeolite sample after the photolysis for 20 h showed a very broad signal centred around $g \approx 2.0$ with a linewidth of *ca.* 1600 G together with a sharp signal at $g \approx 4.3$. The g values and linewidths of the EPR spectra agree with those reported for Fe^{3+} exchanged zeolites.[13] A very sharp signal superimposed on the broad signal at $g \approx 2.0$ was also observed at $g \approx 2.004$ due to $TCNQ^{\cdot -}$ which remained on the surface of the zeolite. Thus, the actual electron source to reduce TCNQ to $TCNQ^{\cdot -}$ may be Fe^{2+} loaded in the zeolite, which is oxidized to Fe^{3+} accompanied by the formation of $TCNQ^{\cdot -}$.

In an MeCN solution, electron transfer from $TCNQ^{\cdot -}$ to Fe^{3+} occurs immediately upon mixing $Fe(ClO_4)_3$ and a sodium salt of

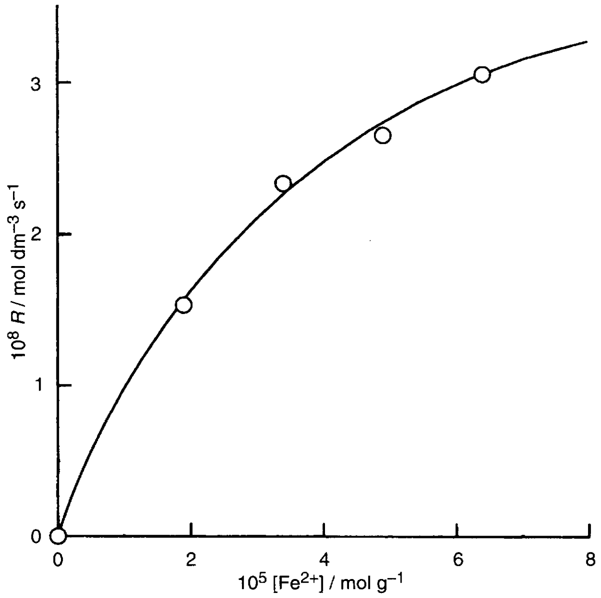


Fig. 1 Dependence of the initial rate of formation of $TCNQ^{\cdot -}$ on the amount of Fe^{2+} loaded in the zeolite, $[Fe^{2+}]$, for the photolysis of the Fe^{2+}–$AcrH^+$–zeolite (20 mg) suspended in an MeCN solution of TCNQ (1.0×10^{-3} mol dm^{-3})

$\text{TCNQ}^{\cdot-}$ which was prepared independently, as expected from the low oxidation potential of $\text{TCNQ}^{\cdot-}$ (0.19 V *vs.* SCE).[14] In order to examine the rate of back electron transfer from $\text{TCNQ}^{\cdot-}$ in solution to Fe^{3+} in the zeolite across the zeolite–solution interface, we prepared the Fe^{3+} exchanged zeolite Y. The rates of back electron transfer from $\text{TCNQ}^{\cdot-}$ in solution to Fe^{3+} in the zeolite were determined from a decrease in the absorption band of $\text{TCNQ}^{\cdot-}$ (λ_{max} 842 nm, ε_{max} 4.33×10^4 $dm^3\ mol^{-1}\ cm^{-1}$).[11] The initial maximum rate of electron transfer from $\text{TCNQ}^{\cdot-}$ (1.5×10^{-5} mol dm^{-3}) to Fe^{3+} (7.5×10^{-6} mol g^{-1}) in the zeolite (20 mg) was only 1.5×10^{-10} $dm^{-3}\ mol\ s^{-1}$, which is orders of magnitude smaller than the rate of formation of $\text{TCNQ}^{\cdot-}$ in Fig. 1. When the amount of Fe^{3+} loaded in the zeolite was increased to 1.5×10^{-4} mol g^{-1}, the initial decay rate of $\text{TCNQ}^{\cdot-}$ was also increased to 2.1×10^{-8} $dm^{-3}\ mol\ s^{-1}$, which is still smaller than the initial rate of formation of $\text{TCNQ}^{\cdot-}$ in the photolysis in Fig. 1. Thus, it has been confirmed that the back electron transfer from $\text{TCNQ}^{\cdot-}$ in solution to Fe^{3+} in the zeolite across the zeolite–solution interface is negligible over a timescale of hours.

The photocatalytic mechanism for the present charge separation system is shown in Scheme 1.

Upon irradiation, photoinduced electron transfer from Fe^{2+} to the singlet excited state of $AcrH^+$ occurs inside the zeolite to yield Fe^{3+} and $AcrH^\cdot$. The free energy change of electron transfer from $AcrH^\cdot$ ($E^0_{ox} = -0.43$ V *vs.* SCE)[15] to TCNQ ($E^0_{red} = 0.19$ V)[14] is largely negative. Thus, electron transfer (k_{et}) from $AcrH^\cdot$ in the zeolite to TCNQ in solution may occur in competition with the back electron transfer (k_b) from $AcrH^\cdot$ to Fe^{3+} in the zeolite. Once $\text{TCNQ}^{\cdot-}$ is formed in solution, the radical anion may be electrostatically repelled by the negatively charged surface of the zeolite, resulting in essentially no back electron transfer across the zeolite–solution interface.[6] By applying the steady-state approximation to the reactive species $^1AcrH^{+*}$ and $[AcrH^\cdot Fe^{3+}]$ in Scheme 1, the dependence of the rate of formation of $\text{TCNQ}^{\cdot-}$ (R) on $[Fe^{2+}]$ can be derived as given by eqn. (1), where I_a is the light intensity absorbed by $AcrH^+$, K_q is the quenching constant

$$R = \{k_{et}[\text{TCNQ}]_a/(k_b + k_{et}[\text{TCNQ}]_a)\}\{I_a K_q[Fe^{2+}]/(1 + K_q[Fe^{2+}])\} \qquad (1)$$

of the singlet excited state of $AcrH^+$ by Fe^{2+} in the zeolite, and $[\text{TCNQ}]_a$ is the concentration of TCNQ adsorbed on the zeolite. From eqn. (1) a linear correlation between R^{-1} and $[Fe^{2+}]^{-1}$ is obtained. In fact, a linear correlation is observed in a plot of R^{-1} *vs.* $[Fe^{2+}]$ using the data in Fig. 1. From the intercept and the slope a K_q value of 2.2×10^4 mol^{-1} g was obtained, in accord with the value (2.5×10^4 mol^{-1} g) obtained independently from the fluorescence quenching of $AcrH^+$ by Fe^{2+} in the zeolite. Such an agreement indicates the validity of Scheme 1.

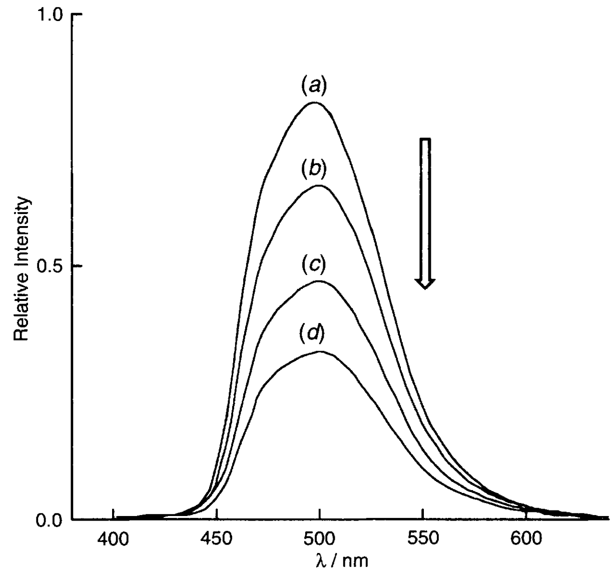
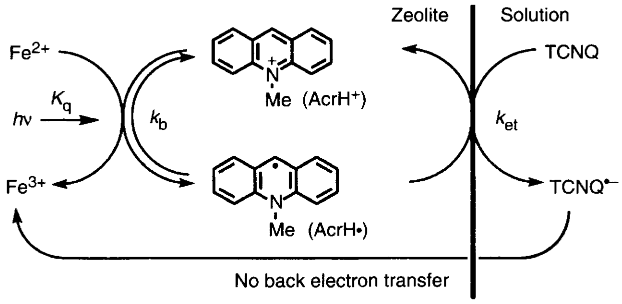


Fig. 2 Fluorescence spectra of the Fe^{2+}–$AcrH^+$–zeolite suspended in MeCN at 298 K; $[Fe^{2+}]$ / mol g^{-1} = (*a*) 1.9×10^{-5}, (*b*) 3.4×10^{-5}, (*c*) 6.4×10^{-5}, (*d*) 9.4×10^{-5}; $[AcrH^+]$ / mol g^{-1} = 1.4×10^{-4}



Scheme 1

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Footnote

† The total amount of Fe^{2+} in Fe^{2+}–$AcrH^+$–zeolite is taken as the sum of the amount of Fe^{2+} contained originally (1.9×10^{-5} mol g^{-1}) and that loaded by the ion exchange.

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