Visual Observation of Salt Migration between Zeolite and Clay in the Solid State

K. B. Yoon* and Y. S. Park

Department of Chemistry, Sogang University, Seoul 121-742, Korea

The formation of highly coloured iodide salts of methylviologen MV^{2+} or diquat DQ^{2+} within zeolites and clay served as an effective visual probe to delineate the phenomenon that NaI salt migration readily occurs between zeolite crystals and between zeolite and clay upon mere physical contact at ambient temperature.

High purity synthetic zeolite crystals are too small to be used as catalysts and adsorbants as such. So they are often blended with natural clays to be formed into agglomerates having high physical strength and attrition resistance.[1] Accordingly, understanding the mass-transfer phenomenon between porous materials is essential for the design and study of zeolites as catalysts and sorption materials.[1,2] However, despite continual emphasis on this phenomenon,[2–6] the study of the inter- and intra-crystalline mass transfer of the zeolite and clay has not progressed to a satisfying degree, presumably owing to the difficulties associated with handling the opaque microcrystalline solids. Such studies become even more difficult when one has to deal with the mass-transfer phenomenon in the solid state.[7]

We now report that the formation of highly coloured iodide salts[†] of methylviologen MV^{2+} and diquat DQ^{2+} within zeolites and clay serves as a remarkable visual probe[8] to elucidate the intercrystalline migration of the intercalated NaI salt upon mere physical contact at ambient temperature.

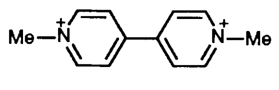
Zeolite-Y, which intercalated approximately one NaI salt in each supercage (average), was prepared by slurrying the rigorously dried sodium zeolite-Y powder [10 g, evacuated at *ca.* 10^{-5} Torr (1 Torr = 133.3 Pa) and 250 °C for 10 h] in an acetonitrile solution of NaI (0.3 mol dm^{-3}, 300 ml).[8] The intercalation of NaI was carried out in a glovebox charged with high purity argon, which was continuously circulated through a drying/deoxygenizing column. The acetonitrile was treated with $KMnO_4$ prior to distillation over CaH_2 and P_2O_5 under argon and stored in a Schlenk flask in the dark. The powder was filtered using a sintered glass filter in the glovebox and subsequently transferred into a Schlenk tube and then evacuated at 100 °C for 10 h to remove the residual acetonitrile. The dried, colourless NaI impregnated zeolite-Y powder (hereafter designated as NaI–ZY) was then transferred back to the glovebox, and aliquots of the sample in small vials were mixed with an equal volume of dry, colourless MV^{2+} or DQ^{2+} exchanged zeolite-Y (*ca.* 0.9 ions per supercage, hereafter designated as MVY and DQY, respectively). The ion exchange of MV^{2+} and DQ^{2+} into NaY was performed in aqueous solutions of $MVCl_2$ and $DQBr_2$, respectively.[8] The air-dried MVY and DQY were washed with copious amounts of methanol and transferred immediately into Schlenk tubes prior to evacuation at 100 °C for 10 h to minimize the residual content of water.

To our surprise, the mixtures readily turned pale yellow (MVY mixture) and orange (DQY mixture) during a mixing period of a few minutes and the colours intensified gradually with aging. The diffuse reflectance spectra of the coloured samples showed well-resolved new absorption bands, with the absorption maxima (λ_{max}) at 380 (MVY) and 400 nm (DQY), respectively. Storing the samples at 80 °C for 1 day, after aging for 3 days at ambient temperature, effected the increase of the absorption with a slight blue shift of the λ_{max}. Fig. 1 illustrates the case of the MVY mixture. Since it is well established[8] that only those zeolite-Y which intercalate sufficient amounts of such highly coloured ion pairs as $MV^{2+}(I^-)$ (yellow) and $DQ^{2+}(I^-)$ (orange) *within* the supercages give colour intensities that are visually detectable, the contact-induced colouration phenomena were attributed to the formation of ion pairs wtihin the zeolite-Y supercages.

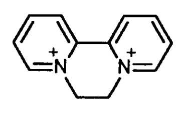
In striking contrast, no such colouration resulted from the ground mixtures of dry NaI salts[‡] (not intercalated, crystalline) and the acceptor doped zeolites even after an extended period of grinding (5–10 min) followed by subsequent aging for more than 6 months at ambient temperature, or standing in an oven at 80 °C for 3 days, as long as they were kept dry.

The two sets of experimental results above lead us to suggest that intercalated NaI is quite different from the crystalline state: being rather molecular[§] and extremely labile (mobile) as if it were dissolved in solvents, it therefore, readily migrates to the neighbouring crystals of zeolite-Y upon mere physical contact at ambient temperature. We believe that the driving force for the intercrystalline diffusion of NaI is provided by the entropy increase in the mixed zeolite system and the formation of charge-transfer salts.

The formation of charge-transfer complexes may also occur by the contact-induced solid-state ion exchange of MV^{2+} and DQ^{2+}.[7] To resolve this ambiguity, a narrow glass tube was packed with NaI–ZY powder (~3 cm) and with MVY powder (~3 cm) on top of the bottom layer in a glovebox. It was then



MV^{2+}



DQ^{2+}

[†] The mono- and di-iodide complexes of MV^{2+} are yellow and red, respectively, and the corresponding complexes of DQ^{2+} are orange and purple, respectively.

[‡] NaI was evacuated at 100 °C for 10 h and stored in a drybox.

[§] From the intercalated amount of NaI as being approximately 1 per supercage, it is suggested that it exists largely in monomeric form.

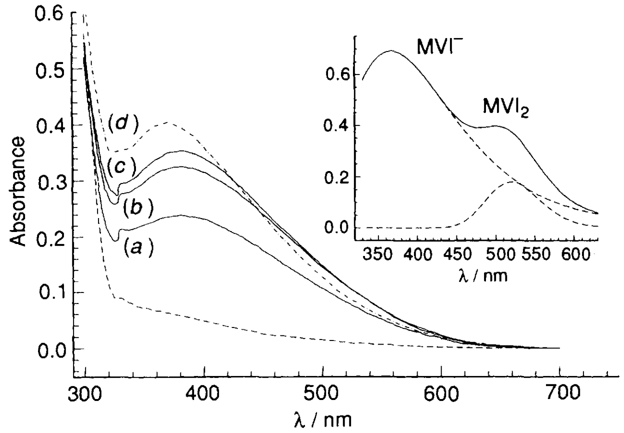


Fig. 1 Diffuse reflectance spectra of the coloured mixture of MVY and NaI–ZY after (*a*) 30 min, (*b*) 1 day, (*c*) 4 days at room temp. and (*d*) after an additional 3 days standing at 80 °C. (The ground mixture of MVY and NAI crystal is shown by a dashed curve.) The inset shows the spectrum of the orange coloured zeolite-Y which contains both the ion pair and ion triplet, from ref. 8.

tightly capped and kept vertically in an oven at 80 °C. A few days later, only the MVY layer turned yellow with gradual diminution of the colour intensity towards the top-end, while the NaI–ZY layer remained colourless. A closer look at the interface also revealed a narrow (≈1 mm) yet intense red band on the MVY layer indicating the presence of red ion triplet $MV^{2+}(I^-)_2$ at the contact zone. The result confirms our conclusion that the NaI salt is indeed the true migrating species.

The solid-state NaI salt migration is also observed between the two different types of zeolite, *i.e.* between zeolite-Y and -L, but at a noticeably slower rate. Intercrystalline salt migration also occurs between the zeolite and synthetic saponite clay. Thus, a mixture of NaI–ZY and MV^{2+} exchanged saponite readily develops a yellow colour at ambient temperature and interestingly, turns orange at 80 °C indicating the formation of the red ion triplet, $MV^{2+}(I^-)_2$, presumably within the interlayer void of the clay. The reverse process, *i.e.* NaI salt transfer from the saponite¶ to zeolite-Y also readily occurs at 80 °C.

It is also important to note that the colouration of the mixtures of NaI–ZY and acceptor-doped zeolite-Y is greatly accelerated when the dry mixtures are exposed to the atmosphere (even briefly) to allow moisture uptake. The ground mixtures of the crystalline NaI salt and the acceptor doped zeolite-Y also readily turn yellow to red (MVY) or orange to purple (DQY) when they are deliberately exposed to the atmosphere, in striking contrast to the dry mixtures. This moisture-induced acceleration of the ion pair and ion triplet formation may arise, in part, by solid-state ion exchange,[7] since similar colouration readily occurs when the crystalline salt of $MVCl_2$ or $MV(PF_6)_2$ is ground together with crystalline NaI either in the presence or absence of moisture.

Although the temperature of 100 °C (above which the doped acceptors are unstable) is not high enough to remove all the water from the acceptor-doped zeolites and clay (the diffuse reflectance FTIR measurements of the dried samples using a special air-tight cell indicated the presence of trace amounts of moisture), the solid-state ion exchange that could be induced by the residual moisture is not important in our dry mixtures since only the MVY layer turns yellow as shown in the above narrow tube experiment and no colouration is observed from the ground mixtures of the crystalline NaI and the acceptor doped zeolites-Y which were dried at this temperature.

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¶ NaI intercalated saponite was prepared by equilibrating saponite in 2 mol dm^{-3} NaI in methanol.