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Iodide-to-cation charge-transfer bands as a novel probe for evaluation of actual acceptor strengths of cations in zeolites and cation-dependent pore volume change

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Iodide-to-cation charge-transfer (ITC-CT) bands have been measured for the first time in zeolites X and Y exchanged with a series of alkali metal ions and the results show that the ITC-CT band progressively red shifts with increasing the size and the number of site III cations in the supercage, which indicates that the actual acceptor strength of the cation toward iodide increases with increasing the degree of protrusion of the cation into supercages and the number of cations, and overall, with decrease in supercage volume.

The charge-balancing cations in zeolites serve as Lewis acid sites for various electron-rich guest molecules. Therefore, gaining insights into the actual acceptor strengths of the cations toward guest electron donors is of prime importance for designing zeolite catalysts and adsorbents for various purposes. One of the possible ways to achieve this goal is to employ appropriate electron donating probes that can induce measurable changes in the physicochemical properties of the system through interactions with the cations located in the pores. As a possible means we have examined iodide as a probe and found that the well-established ITC-CT bands[1] give very useful information that can be utilized to evaluate the actual acceptor strengths of the cations existing in the accessible pores and the cation-dependent pore volume change.

In aqueous solution, iodide shows two absorption bands at 5.5 and 6.4 eV (226 and 193 nm, respectively) at 20 °C, that are much higher in energy than its own ionization potential (3.0 eV).[2–5] Likewise, iodide gives two absorption bands in other solvents that are considerably higher in energy than its own ionization potential. These absorption bands are known as the charge-transfer-to-solvent (CTTS) bands.[2–5] In molten salts, where cations serve as electron acceptors, iodide gives rise to the related ITC–CT bands.[1] The appearance of two bands is ascribed to two different energy states of iodine atom, $^2P_{1/2}$ and $^2P_{3/2}$.[6]

The CTTS band of iodide red shifts as the acceptor strength of the solvent increases in various homologous series.[7] By the same analogy, the ITC-CT band is expected to experience a red shift as the acceptor strength of the cation increases, according to Mulliken theory.[6] Inspired by this interesting phenomenon of iodide, we occluded iodide salts into zeolites X and Y exchanged with various alkali metal cations (designated as M^+X and M^+Y) and measured the corresponding ITC-CT band with the expectation that the ITC-CT band will vary depending on the nature of cation and the resulting variation will provide valuable information about the acceptor strengths of the cations.

For this purpose, we employed zeolites X (Si/Al = 1.3) and Y (Si/Al = 2.6) exchanged with a series of alkali metal ions.[8] Iodide was occluded into each zeolite by equilibrating the rigorously dried zeolite in a methanol solution of each iodide salt for 3 h at room temperature in the dark. The counter cation for iodide was chosen to be the same as the major cation exchanged into the zeolite. The incorporated amount of iodide salt was controlled to be 1 per 40 supercages[9] to prevent saturation of the ITC-CT band during measurements knowing the fact that the molar absorption coefficients of the ITC-CT bands are very high ($> 10^4$ M^{-1} cm^{-1}). The occluded iodide salts are therefore likely to exist in the molecular form rather than be crystalline within the supercages. The iodide-incorporating zeolites were dried by evacuating at 300 °C for 10 h. Among the 10 prototypical zeolites prepared for this purpose, Li^+X, Li^+Y and Na^+Y were discarded since they turned yellow during iodide occlusion, presumably due to oxidation of the incorporated iodide to triiodide by small amounts of acid sites present in the zeolites.[10] The remainder of the dried zeolites were transferred into a glovebox charged with high purity argon and an aliquot of each dried, iodide-incorporating zeolite was transferred into an air-tight flat cylindrical cell for diffuse reflectance UV–VIS measurements (Varian Cary 5).

Fig. 1 shows a series of diffuse reflectance spectra of ITC-CT bands in four different M^+X zeolites with $M^+ = Na^+, K^+, Rb^+, Cs^+$. Among these, M^+X with $M^+ = K^+, Rb^+, Cs^+$ gave two well-resolved ITC-CT bands. The observed ITC-CT bands are proposed to arise mostly from charge transfer from the incorporated iodide to the charge-balancing cations exchanged into the supercages but not to the cations paired to iodide during incorporation.[11] Unambiguous evidence for this proposal is provided from the finding that iodide is produced even from neutral iodine (I_2) upon adsorption onto the highly basic zeolites and the resulting iodide also gives the same ITC-CT bands characteristic of the exchanged cations.[12] Furthermore, even iodide salts with cations different from the major cations exchanged into the zeolite framework also gave the same ITC-CT bands upon incorporation. The latter observation indicates that the occluded iodide salt (M^+I^-) exists in the *dissociated* form ($M^+ + I^-$) within zeolites that can be regarded as solid electrolytic solvents.

The absorption maximums for M^+X were 5.69 (Na^+), 5.23 (K^+), 5.10 (Rb^+) and 4.91 eV (Cs^+) for the low-energy band

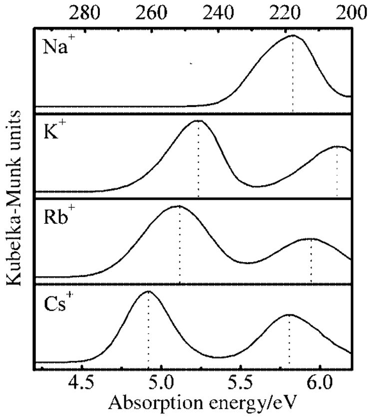

Fig. 1 Diffuse reflectance UV–VIS spectra of iodide in zeolites X exchanged with four different alkali metal ions (as indicated) showing the progressive red shift of the ITC-CT bands with increasing size of the cation.

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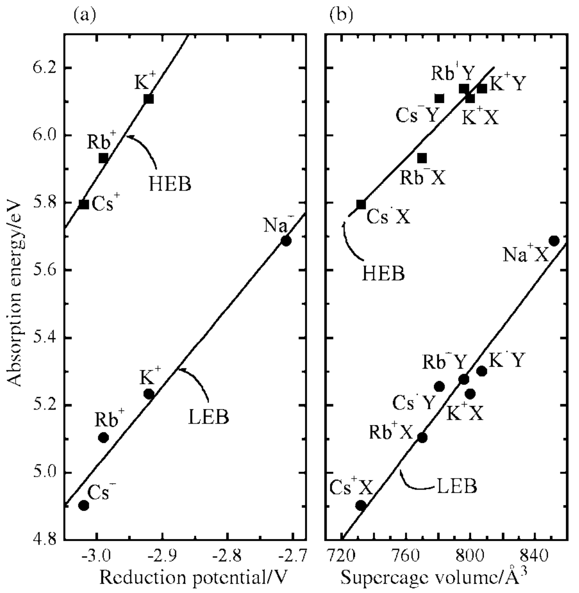

Fig. 2 Linear relationships between the reduction potential of the cation (as indicated) and the absorption energy of ITC-CT bands in zeolite X (a) and between the supercage volume and the absorption energy of ITC-CT bands in M^+X and M^+Y (as indicated) (b), for each high-energy (HEB) and low-energy band (LEB).

(LEB), and 6.11 (K^+), 5.93 (Rb^+) and 5.79 eV (Cs^+) for the high-energy band (HEB). The energy differences between the LEB and HEB were 0.88 (K^+), 0.83 (Rb^+) and 0.89 (Cs^+), smaller than that in water (0.92 eV).[13] This phenomenon may arise due to alteration of the energy difference between $^2P_{1/2}$ and $^2P_{3/2}$ of the iodine atom within the highly polar intrazeolite environments.

The most striking feature to note is that the ITC-CT band progressively red shifts with increasing the size of the counter cation. On the basis of this, we propose that the actual acceptor strength of M^+ increases in zeolite X with increasing size, contrary to the behavior of M^+ in solution. The linear relationship between the electron affinity of M^+ and the ITC-CT band shown in Fig. 2(a) unequivocally demonstrates this contrary behavior of the acceptor strength of M^+ in zeolite X. A similar trend was observed in M^+Y zeolites; 5.30 (K^+), 5.28 (Rb^+) and 5.25 eV (Cs^+) for LEB and 6.14 (K^+), 6.14 (Rb^+) and 6.11 eV (Cs^+) for HEB. The degree of cation-dependent shift is much smaller in zeolite-Y, presumably due to the much smaller number of site III cations within the supercage (~ 1 for Y *vs.* ~ 5 for X).

We believe the increase in the acceptor strength of M^+ with increasing size in zeolites is related to the diminished screening of the cation by the negatively charged framework as depicted in Fig. 3 as the degree of protrusion of the cation towards the center of the supercage increases. In close relation to this, we also discovered an interesting linear relationship between the supercage volume and the absorption energy of the ITC-CT band as shown in Fig. 2(b), regardless of the type of zeolite.[14] This result indicates that the tighter contact between iodide and the cations as a result of the decrease in the pore volume plays a key role for the observed red shift of the ITC-CT band, and hence the actual acceptor strength of the cation. The higher sensitivity in the cation-dependent shift of ITC-CT bands in zeolite X than in Y can also be understood accordingly. We believe the present report is an interesting complement to the CT interaction between iodine and the zeolite framework.[15] Thus, both iodine and iodide serve as probes for the evaluation of the donor strengths of the framework and the acceptor strength of the cation, respectively.

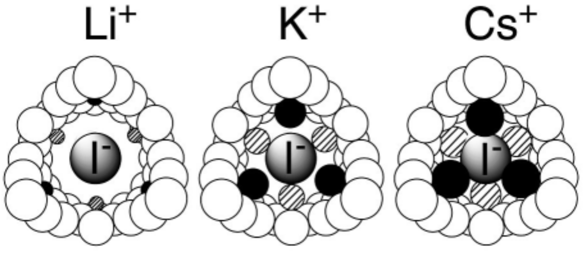

Fig. 3 Pictorial illustration of the reduction in the available space within the supercage of zeolite X as the size of the cation in sites II (hatched circles) and III (filled circles) increases (as indicated).

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Notes and references

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6 According to Mulliken's charge-transfer (CT) theory (R. S. Mulliken, *J. Am. Chem. Soc.*, 1950, **72**, 601), the ground- and excited-state wave functions (denoted as Ψ_G and Ψ_E, respectively) for a donor (D)–acceptor (A) complex are expressed according to the following equations: $\Psi_G = a\psi_0(A, D) + b\psi_1(A^-–D^+) + \ldots$, $\Psi_E = a^*\psi_1(A^-–D^+) - b^*\psi_0(A, D) + \ldots$, where $\psi_0(A, D)$ is the 'no-bond' wave function of D and A and $\psi_1(A^-–D^+)$ is the dative wave function representing transfer of an electron from D to A and $a \gg b$ and $a^* \gg b^*$. Accordingly, if there are two different wave functions for D^+ (iodine atom), there are two different wave functions for Ψ_G and Ψ_E, respectively. However, since $a \gg b$ and $a^* \gg b^*$, there is essentially only one wave function for the ground state whereas there are two different excited-state wave functions. This explains the presence of two ITC-CT bands.

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8 The compositions of the cations in the exchanged zeolites were LiX ($Li_{68}Na_{16}$), NaX (Na_{84}), KX (Na_9K_{75}), RbX ($H_{10}Na_{12}K_{14}Rb_{48}$), CsX ($H_7Na_{12}K_{31}Cs_{34}$), LiY ($Li_{37}Na_{16}$), NaY ($Na_{53}$), KY ($Na_4K_{49}$), RbY ($Na_1K_{16}Rb_{36}$), CsY ($Na_1K_{17}Cs_{35}$).

9 Incorporated amounts were analyzed by Fajans method using tetrabromofluorescein (Eosin Y) as the indicator.

10 Hydrogen iodide is thermally unstable.

11 The possibility of the framework oxygen being the acceptor site is excluded since it is also negatively charged and hence should repel iodide.

12 Elucidation of the interesting phenomenon of reduction of iodine to iodide by electron rich zeolites is in progress and the results will be reported later.

13 The minimum resolution for the UV–VIS spectrometer is 0.03 nm which corresponds to a minimum accuracy of the measurement of 0.001 eV (at 200 nm).

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