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Zeolites

Electrochemically Controlled Ion Exchange: Proton Exchange with Sodium Zeolite Y**

*Michael J. Stephenson, Stuart M. Holmes, and Robert A. W. Dryfe**

In memory of R. J. Plaisted

Zeolites are central to a number of industrially important processes, such as catalysis, gas separation, and sorption of impurities from the solution phase.[1,2] All zeolite structures, other than the purely silicaceous series end-members, contain counterions, whose nature and position can be extremely important in the aforementioned applications. Catalytic cracking of hydrocarbons, for example, is dependent upon the introduction of protons to the zeolite structure.[3] Since zeolites are frequently synthesized in their sodium form, other counterions must be introduced through ion exchange.

Zeolite Y, which has the Faujasite structure, is a principal component of cracking catalysts because of properties such as its high thermal stability and large internal surface area with easily accessible active sites. It consists of a 3D network of 12 Si or Al atoms that form circular channels 7.4 Å in diameter with cavities 11.8 Å in diameter.[4] The as-synthesized sodium form is converted into the acidic form either by direct ion exchange with dilute mineral acids or by calcination of the ammonium ion exchanged form of the zeolite to release

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[*] Dr. M. J. Stephenson, Dr. R. A. W. Dryfe
School of Chemistry
University of Manchester
PO Box 88, Manchester, M601QD (UK)
Fax: (+44) 161-200-4559
E-mail: robert.dryfe@manchester.ac.uk

Dr. S. M. Holmes
School of Chemical Engineering and Analytical Science
University of Manchester
PO Box 88, Manchester, M601QD (UK)

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ammonia.[5] Care is needed with direct ion exchange because at low pH values acid-mediated dealumination occurs followed by structural collapse.[6] To avoid these problems, the route from the ammonium ion exchanged form to acidic zeolite Y (H−Y) is preferred. Herein, we demonstrate a novel, direct method for the preparation of H−Y by electrochemically controlled proton exchange. Importantly, we believe this method, which offers enhanced control over the degree of ion exchange, is generic, and is thus applicable to other zeolite structures and the introduction of other cations.

The novel approach described herein is derived from liquid/liquid electrochemistry, in which ions can be driven from one liquid phase into an adjacent immiscible liquid phase by application of a potential across the liquid/liquid interface.[7,8] Typically, an aqueous/organic system is employed, with solvents such as nitrobenzene or 1,2-dichloroethane (DCE) used as the organic phase. The transfer of hydrophilic ions, such as Na^+, can be facilitated by the use of a complexing agent in the organic phase (for example, crown ethers). This complexing agent stabilizes the transferred ion, and in doing so lowers the required transfer potential [see Equation (1), in which the equilibrium is potential-dependent and L denotes the complexing agent].

$$Na^+_{(aq)} + L_{(org)} \rightleftharpoons [Na^+{-}L]_{(org)} \qquad (1)$$

Judicious choice of the complexing agent and organic solvent allows the selective transfer of ions from multi-ion aqueous solutions; for example, small crown ethers are more selective for small ions[9] and thioethers are more selective for transition metals.[10,11] Selective ion transfer at nonpolarized liquid/liquid interfaces is utilized for specific metal extraction (for example, electrorefining and hydrometallurgy).[12] Herein, selective ion transfer at an electrified interface is used to remove unwanted ions from the exchange medium, which in turn drives the equilibrium towards further ion exchange of the zeolite with the required counterion. With reference to Equation (2), the removal of Na^+ ions from the aqueous phase will shift the ion-exchange equilibrium to the right, which increases the amount of H^+ ions in the zeolite.

$$Na^+_{(zeolite)} + H^+_{(aq)} \rightleftharpoons H^+_{(zeolite)} + Na^+_{(aq)} \qquad (2)$$

This method allows excellent control over the composition of the exchange medium, and hence exerts control over the extent of ion exchange (see Figure 1 and the Experimental Section).

The exchange process within the zeolite is predicated on its ability to sequester Na^+ ions in the organic phase with dibenzo[18]crown-6 (DB18c6). The electrochemically induced transfer of Na^+ ions occurs at a lower potential than that of H^+ ions (Figure 2). The voltammetric analysis shows that the maximum current required for the transfer of Na^+ ions is observed at an applied potential difference $\Delta\varphi$ of 0.60 V, whereas the peak current for the transfer of H^+ ions is seen at $\Delta\varphi = 0.73$ V. Therefore, if $\Delta\varphi = 0.60$ V across the exchange medium/organic interface, the transfer of Na^+ ions will be favored over the transfer of H^+ ions by a factor of $\exp(zF(0.13)/RT) \approx 150$.[7] A typical time-dependent current response is shown in Figure 3 in which $\Delta\varphi = 0.60$ V across the interface. The resultant current is essentially caused by the transfer of Na^+ ions across the interface; from the magnitude of the charge passed, the amount of Na^+ ions extracted can be calculated by using Faraday's law. In this way, the removal of sodium from the exchange medium can be controlled, thus exerting control over the extent of ion exchange within the zeolite.

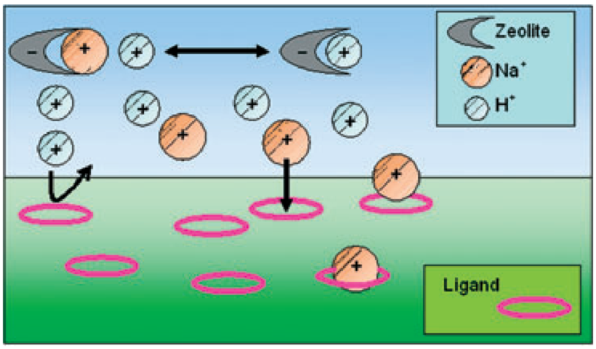

Figure 1. A schematic diagram of ion exchange in a zeolite suspended in an aqueous phase (aq) with the selective extraction of Na^+ ions into an organic phase (org), which forces the ion-exchange equilibrium [Eq. (2)] over to the right (protonated form of the zeolite).

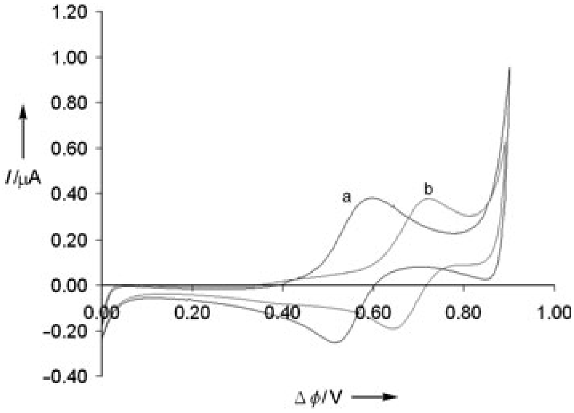

Figure 2. The cyclic-voltammetric data showing comparative transfer of Na^+ and H^+ ions facilitated by DB18c6 using a) cell 2 and b) cell 1 (see the Experimental Section) with a voltage scan rate of 0.1 Vs^{-1}.

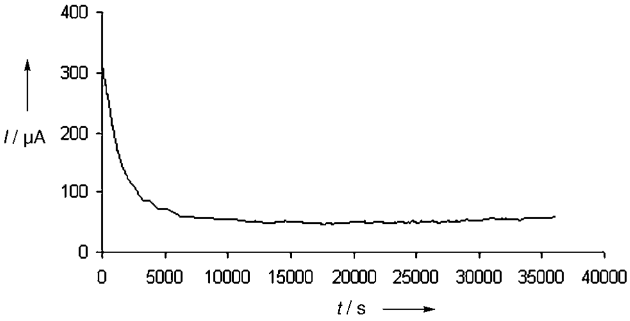

Figure 3. Chronoamperometric response of cell 3 (see the Experimental Section; X = acetic acid). The potential was stepped from 0.1 to 0.6 V and held at 0.6 V for 10 h.

The sodium and aluminum contents of the zeolite samples were then determined by inductively coupled plasma atomic emission spectroscopy (ICPAES). The proton concentration was calculated indirectly by mass balance [Eq. (3)]:

$$|H^+|_{zeo} = |AlO_2^-|_{zeo} - |Na^+|_{zeo} \tag{3}$$

The equivalent fractions of H^+ ions in the zeolite E_H, as measured experimentally, were plotted versus the charge transferred across the interface (Figure 4). The equivalent fraction for ion A (E_A) was calculated with Equation (4), in which z_A is the valency of ion A, n_A is the number of moles per unit mass, and M_t is the exchange capacity of the zeolite.)

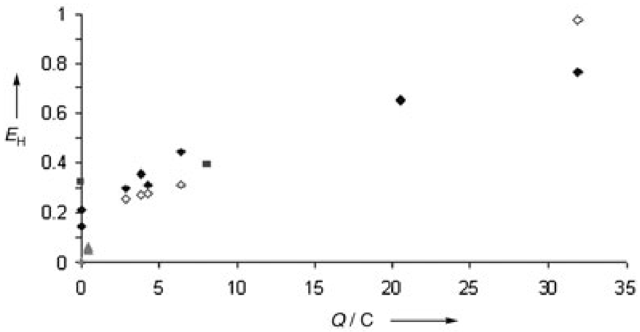

Figure 4. Graph of E_H values versus the total charged passed (Q): E_H was measured by ICPAES. Cell 3 was used (see the Experimental Section), in which X is acetic acid (filled diamonds), sulfuric acid (squares), or pure water (triangles). Data predicted by the calculations, as described in the text, are denoted with open diamonds.

$$E_A = \frac{z_A n_A}{M_t} \tag{4}$$

The values obtained at zero Coulombs relate to the chemically exchanged samples in pure water (A), 0.02 M acetic acid (B), or 0.01M sulfuric acid (C). These samples were left to pre-equilibrate with the zeolite for at least 14 days and were the starting points for the electrochemical experiments. Samples of type B were analyzed again after the electrochemical experiments had been completed (after approximately 2 months). For samples of type A, no proton exchange was detected after only the chemical exchange had been carried out. Subsequent electrochemical studies using pure water were hampered by resistance resulting from the aqueous phase, which made it very difficult to remove the Na^+ ions. However, partial dissociation of water allowed some H^+ ions to be incorporated, which permitted a maximum of $E_H = 0.07$ to be obtained. Note that no cations, other than H^+ ions, were present in any of the aqueous phases of the cell. For samples of type C, $E_H = 0.33$ after the chemical exchange and increased to 0.39 after 8 C of Na^+ ions had been removed from the exchange medium. For the samples of type B, $E_H = 0.15$–0.20 after the chemical exchange, which is lower than the level achieved with the sulfuric acid sample (C) and is attributed to the partial dissociation of acetic acid. However, the use of a sulfuric acid solution (C; pH = 2) might have a detrimental effect on the zeolite structure through dealumination.[13] The acetic acid solution was found to be well suited to these studies because it was sufficiently conductive to be used as an electrolyte, but was not too acidic; acted as a good source of H^+ ions; and behaved as a buffer, because it is a weak acid, giving a constant pH value of approximately 4. Figure 4 shows that there is a significant increase in the extent of the proton exchange, with increasing charge being passed. The E_H value rose to 0.77 after 32 C of Na^+ ions were extracted from the exchange medium; it is likely that this value could be improved with continual removal of Na^+ ions.

In the above experiments, it was assumed that the ion exchange was being chemically driven by transferring unwanted Na^+ ions from the exchange medium into the organic phase [Eq. (1)], which then shifts the ion-exchange equilibrium to the right [Eq. (2)]. It is conceivable that the application of an electric field at the interface may alter the ion-exchange equilibrium or remove ions directly from the zeolite; if this effect is significant, then the extent of the ion exchange will differ from that of the isotherm based just on the chemical ion-exchange process. An attempt was made to predict the extent of the ion exchange using the corrected selectivity quotient for the chemical equilibrium and the changes measured in the composition of the exchange media after electrochemical removal of the Na^+ ions (Figure 4). These predictions were then compared to the experimentally derived zeolite compositions (see the Supporting Information). The experimental values of E_H are slightly greater in most cases than the predicted values, which suggests that an electrochemical enhancement of the ion-exchange process occurs. The predicted value at 32 C is greater than the experimental value; this difference is probably because the transfer of H^+ ions begins to contribute significantly to the charge transfer at this point. At higher levels of proton exchange, the exchange medium contains a very low concentration of Na^+ ions and the selectivity of the transfer of Na^+ ions decreases, which means significant transfer of H^+ ions occurs with the transfer of Na^+ ions. However, the calculations are approximate as the corrected selectivity quotients only allow for the nonideality of the solution[13–15] and not the zeolite and only the aluminum and sodium contents are known as they are measured directly. A more accurate calculation based on the electrochemically enhanced exchange of copper ions in NaY is underway, in which both the outgoing and incoming ions can be measured directly.

The structural integrity of the samples after either chemical exchange or electrochemically enhanced ion exchange was assessed by X-ray diffraction (XRD) and N_2 sorption/desorption measurements. Exposure of samples to acid (types B and C) did not lead to the formation of amorphous regions in the XRD patterns or to any significant loss of crystallinity. The N_2 sorption isotherms showed no evidence of hysteresis, thus indicating that no secondary pore system had been formed. Secondary pores may develop with acid-induced degradation.[16] For type B samples, Barrett–Joyner–Halenda (BJH) calculations[17] of the pore-size distribution showed no significant change relative to the fresh sample. However, type C samples developed some pores approximately 100 Å in diameter following two weeks of exposure to acid. Brunauer–Emmett–Teller (BET) surface-area measurements revealed an approximate decrease in the internal surface area for the chemically exchanged samples of type C, compared to the fresh sample after two weeks of exposure to sulfuric acid; $E_H = 0.3$ after two weeks. For type B samples, both the extent of the ion exchange and the change in the surface area were small following two weeks of exposure to acetic acid. However, extraction of 2.8 C of charge from this sample caused the E_H value to rise to 0.3. Significantly, the amount of H^+ ions needed to achieve this rise could be introduced into the sample with a decreased level of concomitant change (ca. 10 %) in the surface area, as measured by BET studies, compared to the type C samples.

In summary, ion exchange can be readily controlled in microporous materials through the use of electrified interfaces: protons can be incorporated into these materials using weak acids, without the need for repeated washing. Therefore, this method is very useful for zeolites that are pH sensitive. We are currently applying this technique to zeolites with high aluminum contents, that is, NaA and NaX. This new method is very effective at removing small concentrations of unwanted ions from exchange media, and so is able to complete the exchange more efficiently than repeated washing. The exchange of ions with poor selectivity also benefits from this method, as small traces of unwanted counterions can be removed and there is no need to continually refresh the exchange medium; furthermore, the direct ion exchange of preformed membranes that are sensitive to thermal treatment is allowed. This phenomenon has been found to be useful in the final stages of copper(II) ion exchange with NaY. In addition, judiciously chosen complexing agents allow the electrochemically enhanced ion exchange of nearly every possible combination of ions. The tertiary Li^+/Ca^{2+}/NaX system is also currently being studied. The preliminary data reported herein suggest that the electrochemically enhanced ion-exchange process yields greater ion exchange than would be expected from just a chemical exchange.

Experimental Section

Method: The zeolite powder (2.5 wt % NaY; Crossfield Chemicals, Warrington, UK) was suspended in the aqueous phase of the cell (cells 1–3). The Na^+ ion content of the as-purchased zeolite sample was greater than 98 %; the remaining ions were protons. ICPAES analysis was performed on the fresh sample, the level of the initial proton impurities was below the experimental error of ICPAES. The water/DCE interface was supported within a polyethylene terephthalate "track-etched" membrane (0.1 μm pore diameter; Osmonics Inc., Livermore, CA, USA). The organic phase electrolyte in all cases was bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluoro)phenylborate (BTPPA $TPBF_{20}$). The water/DCE interface was polarized using a four-electrode potentiostat (Autolab PGSTAT 100; Eco-chemie, Utrecht, Netherlands). The organic phase was stirred at 4 Hz with a magnetic stirring device; other cell details have been reported previously.[18] For these experiments, the organic solution was renewed every 10 h. Typical currents were approximately 50 μA, which could be increased by using a higher interfacial area and/or by stirring both phases. The experiments were performed at ambient laboratory temperature (293(±)2 K).

The electrochemical cells used can be written as:

Cell 1

$Ag_{(S)}|AgTPB_{(S)}|0.02\,\text{M}$ $BTPPATPBF_{20}$, $1\times10^{-3}\,\text{M}$ $DB18c6_{(DCE)}||$ $0.01\,\text{M}$ $H_2SO_{4(aq)}|Ag_2SO_{4(S)}|_{Ag(S)}$

Cell 2

$Ag_{(S)}|AgTPB_{(S)}|0.02\,\text{M}$ $BTPPATPBF_{20}$, $1\times10^{-3}\,\text{M}$ $DB18c6_{(DCE)}||$ $0.01\,\text{M}$ H_2SO_4, $0.01\,\text{M}$ $Na_2SO_{4(aq)}|Ag_2SO_{4(S)}|_{Ag(S)}$

Cell 3

$Ag_{(S)}|AgTPB_{(S)}|0.02\,\text{M}$ $BTPPATPBF_{20}$, $0.01\,\text{M}$ $DB18c6_{(DCE)}||$ 2.5 wt % NaY, $0.01\,\text{M}$ $X_{(aq)}|Ag_2SO_{4(S)}|_{Ag(S)}$

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