The structural change of intercalated iodine determined by the inner surface properties of ion-exchanged zeolite A

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Abstract

The inner-surface properties of zeolite A (LTA) were modified by the exchange of the charge-balancing non-framework cations (Li^+, Na^+, K^+, Rb^+, and Cs^+). Molecular iodine, sorbed from the vapor phase, was used to probe these properties. The structure of molecular iodine, introduced via the vapour phase, is changed by these surface properties. Our results, based on techniques allowing access to the geometric (X-ray absorption fine structure), electronic (UV–Vis spectroscopy) and vibrational structure (Raman spectroscopy) of the iodine molecule show that the intercalated molecules located at the inner surface of the zeolite are strongly influenced by the electric fields determined by the cations (Li^+, Na^+, K^+, Rb^+, and Cs^+). EXAFS and UV–Vis spectroscopy reveal changes in the average bond distances and the electronic structure. Interestingly, in Rb- and Cs-exchanged zeolites, triiodide anions are apparently formed. Since all of the observed changes can be related to the cations present in the cages, we can thus demonstrate that iodine is influenced by the inner surface properties of zeolites.
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1. Introduction

The inner surface of a zeolite material determines the reactivities of the host framework and also influences the optical properties of guest components. In this work the aluminosilicate LTA (also known as zeolite A) serves as a host system. The chemical composition of a zeolite and its surface properties are functions not only of the chemical make-up of the framework, but also depend on the charge-balancing framework cations M (of valence n) in the general formula $M_x[(AlO_2)_x(SiO_2)_y]mH_2O$. Within their pore systems zeolites, can accommodate a wide variety of guest species, including neutral molecules and charged ions [1]. Due to this property, the traditional applications of these microcrystalline hosts are in the areas of ion-exchange, separation, and catalysis [2].

The typical reactivity of zeolites in catalytic reactions is acidic, for example in industrially important cracking processes. The acidity is usually obtained by introducing NH_4^+ ions and subsequent removal of NH_3. However, by ion-exchange with alkali cations, also a basic reactivity can be generated, which can be utilized in catalytic reactions (such as the alkylation of toluene with methanol). The basicity increases of either the framework or the countercation, individually or in combination, with the electropositivity of the exchange cation [3–5]. Commonly, the basic sites in alkali-ion exchanged zeolites are characterized by IR spectroscopy or by the desorption of adsorbed probe molecules, such as carbon dioxide [5–10], pyrrole [11–13] or chloroform [14–16].

Another interesting probe molecule is I_2. It has been known for some time that iodine is a molecular probe of

electron donor strength [17,18], and that the adsorption of iodine in zeolites is possible [19,20]. More recently, Yoon and co-workers investigated iodine insertion compounds of zeolites (LTA, FAU, ZSM-5, LTL, MAZ, and MOR) exchanged with different alkali-ion cations. They found a blueshift in the UV–Vis absorption bands of the adsorbed iodine with increasing electropositivity of the non-framework cation and the aluminium content in the framework. Therefore, the blueshift can be used as a measure for the donor strength of zeolite frameworks [21]. Davis and co-workers probed the basicity of alkali-metalion exchanged zeolites X and Y by diffuse reflectance UV–Vis spectroscopy of adsorbed iodine. The observed blueshift correlated with the negative charge on the framework oxygen atoms [22]. In contrast, when, instead of charged aluminosilicate hosts, neutral frameworks, consisting of pure silica, are used (so-called zeosils), i.e. when ionic interactions are absent, then the electronic properties of the inserted iodine molecules are influenced mainly by the restrictions of the geometrical arrangement of the guest molecules as imposed by the pore structure of the host framework [23].

In this work, we investigate the iodine insertion compounds of the aluminosilicate zeolite A (framework topology LTA) [24–26] exchanged with different alkali-metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+). We employ techniques addressing the electronic (UV–Vis spectroscopy), and vibrational (Raman spectroscopy) and also the geometric structure (X-ray absorption) of the probe molecule. These measurements reveal the identity of the iodine molecules located inside the zeolite's interior, provide bond-length data on them and show the influence of electric fields exerted on them by the zeolite framework and the non-framework cations.

2. Experimental

2.1. Compounds

Zeolite A (Na-LTA) was synthesised as described by Calzaferri and co-workers using a sol–gel procedure that involves the preparation of two solutions ('A' and 'B'); 'A' containing 7.721 g tetraethyl orthosilicate (Fluka) solved in 150 g aqueous solution of 5.85 g NaOH. 'B' containing 2 g metallic Al (Merck) prepared by solving the Al in 150 g aqueous solution of 5.85 g NaOH [27]. Solution (A) is stirred for 3 h at 60 °C, solution (B) for 3 h at 90 °C. Both solutions are cooled to 25 °C and 'A' is added to 'B' under vigorous stirring. After 15 min the solution was heated and stirred for 16 h at 90 °C in an argon atmosphere. The solid was separated from the supernatant by decantation and washed with NaOH solution 3 times and then with water until the pH of the filtrate was 7.5. The zeolite was dried overnight at 120 °C.

2.1.1. Ion-exchange

Lithium-, potassium-, rubidium- and caesium-exchanged zeolites were obtained by ion-exchanging Na-LTA in a 1 M of the corresponding nitrates (Aldrich, 99.9%). The zeolite was stirred for 24 h at 20 °C The exchange procedure was repeated three times. Then the ion-exchanged samples were washed three times with water and dried at 40 °C.

2.1.2. Iodine-insertion

The ion-exchanged samples were dehydrated at 500 °C (10^{-5} mbar) for 4 h in a quartz tube. The iodine (dried by gentle heating under vacuum) insertion was carried out in an evacuated quartz-glass tube (10^{-5} mbar), using a separate reservoir containing crystalline iodine (Fluka, 99.5%). The reaction took place at 110 °C for 3 days. The samples turned bright and colourful after being exposed to iodine vapour. The excess of iodine on the zeolite surface was removed by sublimation at 40 °C.

2.2. Characterization

The compositions of the ion-exchanged zeolite A samples and of the insertion compounds were obtained by thermal analysis using a Mettler thermo-analyser with an argon flow of 5 l/h and a heating rate of 6 °C/min over the temperature range 30–900 °C. The concentrations of alkali ions were measured with a Hitachi Z 6100 atomic absorption spectrometer (AAS). The samples were dissolved in HCl. The UV–Vis spectra were recorded in diffuse reflectance mode using a CARY 17E spectrophotometer, pure Na-LTA was used as a white standard. The samples were diluted (1:10) with Na-LTA and cooled to 10 K for recording of the spectra. Raman spectra were obtained with a DILOR OMARS 89 spectrophotometer. The Ar-laser-beam (19435.2 cm^{-1} line at 5 mW power at 300 K) was focused on a single crystal (3 μm) for 2×500 s.

Samples for X-ray absorption spectroscopy were pressed in polyethylene pellets at concentrations sufficient to provide increments in X-ray absorbance at the edge ($\Delta\mu d$) of 0.5–0.8. The samples were cooled with liquid nitrogen to 77 K. Extended X-ray absorption fine structure (EXAFS) spectra were measured on beamline X1 at HASYLAB (DESY/Hamburg/Germany) using synchrotron radiation from the storage ring DORIS-III (4.445 GeV at a current of 145 mA). Absorption spectra were measured in transmission mode (Si(3 1 1) double crystal monochromator, 70% detuned). Data processing was done using WinXAS [28] for data reduction and fitting. Feff 7 [29] was used for calculation of theoretical phases and amplitudes. The spectra were calibrated, background-subtracted and normalized. A cubic spline function was applied to remove the background and obtain EXAFS data in k space. The Fourier transformation to R space was performed using a Bessel function in the range 3–14.7 Å^{-1} (13.5 for K-LTA). Theoretical calculated phase shifts and amplitudes were fitted to the experimental function in k and R space. KI, RbI and I_2 (all from Fluka) were used as references.