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Influence of zeolite acidity on proton conductivity of FAU embedded imidazole

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ABSTRACT

Imidazole entrapped in H-forms of FAU zeolites with various Si/Al ratios (1, 4, 40) exhibit high and stable proton conductivity (up to $\sim 10^{-3}$ S/cm) in a broad range of temperatures (293–393 K). The conductivity increases with temperature and imidazole loading. The number and strength of zeolite acid sites (resulting from various Si/Al) influence markedly the conductivity of composites. The samples based on zeolites with low Si/Al (1) show markedly higher conduction than these supported on the matrix with medium Si/Al (4), regardless of very similar number of the acid OH groups. The strong acid OH groups in zeolite with Si/Al = 4 result in protonation and immobilization of adsorbed imidazole, which reduce their mobility and subsequently the conduction. The low siliceous with weaker acid sites protonate imidazole and form a chain of H-bonds effective in proton propagation. Almost neutral high silica matrix provides a high mobility of dispersed imidazole, due to weak mutual interaction. The overloaded samples indicate a phase transition effect at elevated temperature due to melting of extra-matrix imidazole, which is reflected in dramatic increase in conductivity.

1. Introduction

Imidazole (Im) due to its polar nature, high dipole moment, high amphotericity and ability to form the hydrogen bonds may be considered as a potential suitable component of solid proton conductors [1–3], prerequisite for efficient operation of fuel cells at elevated temperatures [4,5]. Conventional solid electrolytes (e.g. hydrated polymers like Nafion) lose their high conductivity after thermal removal of water responsible for propagation of protons. Humidification of the system is costly and troublesome. Imidazole (b.p. 530 K) may replace water in proton propagation particularly at elevated temperatures [6]. The imidazole does show very low conduction ($\sim 10^{-8}$ S/cm) in solid state because of limited mobility of molecules inside the crystalline structure [1,7,8]. Moreover, the experiments with tracers [9] and the results of ^{15}N NMR measurements put in doubt any existence of proton conduction of very pure, crystalline imidazole [10]. Im, however, shows appreciable conduction after melting ($\sim 10^{-3}$S/cm) or dispersing in porous matrices [1]. Imidazole and its derivatives (e.g. benzimidazole) as well as other heterocycles, such as pyrazole, were studied by Kreuer et al. as proton solvent in proton-exchange membranes (PEMs) for fuel cells [4]. The authors have found that the transport coefficients (i.e. mobility of protonic charge carriers and molecular diffusion coefficients) were similar to those of water at temperature relative to the respective melting point [11]. There are already numerous published reports on imidazole composites with various matrices (e.g. MOFs [12–16], porous silica [17], polymers [18–21]), that exhibit remarkable proton conduction. The presented opinions concerning the influence of chemical nature of matrices on conductivity of embedded Im are often ambiguous. Some authors claim that presence of polar groups and resulting hydrogen bonds retards the Im conductivity [18,22], because of diminished molecule motion, whereas other papers demonstrate increased conductivity due to contribution of the matrix protogenic groups [4,16,17,22]. There are interesting attempts to explain the mechanism of proton conduction of solids by studying the analogous liquid systems.

For instance Kreuer et al. [23] examined the effect of adding imidazole to H_2SO_4 and H_3PO_4. In the case of H_3PO_4 admixture of Im resulted in the conductivity decrease, while the low content of Im admitted to H_2SO_4, increases dramatically its conduction. The proton conductivity decrease was explained by removal of protons from the H-bonded network in H_3PO_4 and subsequent formation of very stable H-bonded ion pairs. The authors also suggested that the imbalanced number of proton donors and acceptors in pure H_3PO_4 enabled the oxygen atoms to act as both donors and acceptors. This leads to formation of fragile and breakable H-bonds involved in the reorientation and reorganization of the H-bonded network. Thus, adding of imidazole

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reduces number of proton donors and increases content of acceptor sites. It renders the H-bonded network too stable to favor the Grotthuss mechanism. The increase in the conductivity of H_2SO_4 by doping with Im is explained by water like behavior of Im and raising number of proton defects.

Regarding the above finding Schechter and Savinell attributes the increase in conductivity of H_2SO_4 after adding some Im rather to a neutralization of adverse remnants of SO_3 usually present in the concentrated acid [24]. Elimination of SO_3 leads to enhanced H_2O/H_3O^+ concentration, which is beneficial for the conductivity. In the case of phosphoric acid, where no P_2O_5 is present in acid, the influence of added Im was not recorded.

Pu and Wang observed that addition of Im into the H_3PO_4 doped polyimide membrane not only increased its conductivity, but also improved the stability of chemical oxidation [25]. Experimental investigations have supported the proton transport in imidazole and its derivatives via the Grotthuss mechanism. In contrast, Hickman et al. concluded by means of the results of solid-state N^{15} NMR, that proton tunnelling is responsible for conduction in solid crystalline imidazole [26].

We noticed a high conductivity of imidazole entrapped both in polar H-zeolite (e.g. HL) as well as in neutral AlPO-5 matrix [27].

Zeolites were broadly studied as potential, promising proton conductors in the presence of adsorbed water [28–30] or ammonia [31]. Variety of zeolite structures with different types of pores (e.g. channels, cavities, one-, two- or three dimensional pore systems) and assorted chemical composition allow to tailor the properties of resulting composites in a broad range. Negatively charged aluminosilicate framework of zeolite structure is compensated by the extra-framework cations (mostly alkaline). The cations are easily exchangeable. Therefore, zeolites are very broadly applied as very efficient cationic exchangers. The proton can be also introduced into zeolites as a cation compensating the framework negative charge. The H-form of zeolites are mostly prepared by means of ion-exchange with NH_4^+ cations, followed by thermal decomposition of resulting ammonium cation into gaseous ammonia and proton. This protonic zeolites are very strong solid Broensted acids and they resemble mineral acids in some aspects (e.g. in catalysis). It is well known that the low siliceous zeolites are more hydrophilic that those with high Si/Al, but, on the other hand their H-forms show lower acid strength [32].

The molecular sieve effect of zeolites provides a selective adsorption of molecules with respective size. Adsorbed molecules exhibit very high, almost molecular dispersion.

We consider a substantial impact of zeolite matrices on interaction with the Im guest molecules and on the resulting conduction ability. In neutral matrices (i.e. AlPO, silicalites or highly siliceous zeolites) only a weak van der Waals' interaction can be assumed, therefore the guest molecules have a liberty to move freely inside the pores and act as efficient proton carriers. Whereas in the polar hydrogen forms of zeolites (with acid sites) adsorbed Im molecules undergo a protonation and the resulting Him cations become firmly attached to negatively charged zeolite framework by means of strong ionic bonds. In this case a translating mobility of the guest molecules is substantially reduced, which hinders the proton conduction proceeding according to the vehicular mechanism [33]. On the other hand, the attached Him cations can form a chain of hydrogen bonds and effectively contribute in a transportation of protons by means of the Grotthuss-like manner [28]. It is also possible that both mechanisms are involved [34]. The conductivity of anhydrous H-forms of zeolites is very low, because a distance between adjacent OH groups is too great to provide a formation of hydrogen bonds and subsequently a migration of protons. An introduction of Im molecules into the system acts similarly as adding water to anhydrous H-zeolites, which means the protons react with imidazole and form the chain of hydrogen bonds. The conductivity of imidazolium cations could be even enhanced, when the number of introduced Im species exceed the number of zeolite acid OH groups. The introduced neutral Im molecules could promote the conduction of the adjacent Him cations similarly as water or ammonia molecules in hydrated zeolites [28,33]. The zeolite matrices can also provide the Lewis - type acid sites as well as cations (e.g. transition metal cations) prone to form coordinative bonds with donors of electron pairs (e.g. imidazole) and anchor these guest molecules [35]. The conductivity of Im composites can be markedly affected by the interaction of this kind. Our preliminary experiments indicated that the sample containing Im introduced into zeolite Y with Lewis acid sites showed much lower conductivity than that based on zeolite HY (with Broensted centers) [36].

Versatility of potential interactions should be reflected in different conductive properties and study on that could find a practical meaning and provide broader explanation of the nature of this process.

Here we choose the hydrogen forms of equal structure of synthetic zeolite of faujasites type with different framework Si/Al ratios such as low siliceous zeolite X (with Si/Al ~1), medium siliceous, dealuminated zeolite Y (Si/Al ~4) and highly siliceous USY (Si/Al = 40).

Regardless of practically the same crystalline (FAU) and porous structure of chosen zeolites their properties (e.g., number and strength of acid sites) differ regarding the framework Si/Al ratio. Elucidation of the impact of different acidity of applied faujasite matrices on properties (particularly conduction) of the resulting Im composites is the main aim of this study. We also examine the influence of Im loading on conductivity and on behavior of the resulting composites.

2. Experimental

Commercial zeolites with FAU structure such as: Na LSX (low silica zeolite, Si/Al = 1, Praxair, No.16193–42), DNH_4Y (medium silica, ammonium form of dealuminated zeolite, Si/Al = 4.25, Katalistiks), HY CBV780 (high silica zeolite, Si/Al = 40, Zeolyst) were applied as starting materials. Sodium form of LSX was modified by ion-exchange with NH_4Cl aqueous solution (0.1 M) three times. The resulting ammonium modifications of LSX as well as DNH_4Y were thermally (623 K, 12 h) transferred into hydrogen forms. The composition was determined by means of elemental analysis. The resulting hydrogen forms applied as matrices were labelled as following: LS (low silica), MS (medium silica) and HS (high silica).

The above zeolite samples were also thermally activated (at 623 K, 5 h) right before the impregnation with Im solution in order to remove the adsorbed water. Then after cooling they were treated with chloroform solutions of imidazole (Sigma–Aldrich). Zeolites (1 g) were immersed in imidazole chloroform solutions (3 ml) of various concentration (corresponding to the chosen loading range 0.21–0.35 wt fraction of Im). Imidazole loading in resulting composites is shown in Table S1. The maximum potential Im loading was estimated by calculation the number of imidazole molecules required for filling the volume of the inner voids of faujasite unit cell [27]. The resulting suspensions were kept in closed vials at room temperature for 24 h. Then the solvent was gradually evaporated under continuous stirring at 323 K until a smell of chloroform was noticeable. The solvent evaporation did not affect the desired Im content in the resulting samples, which did not indicate any notable deviation from the results of elemental analysis.

The obtained composites were labelled according to the following scheme: zeolite matrix@Im loading (wt. fraction), for example: HS@0.3Im, which means: high siliceous zeolite containing 30 wt % of Imidazole.

The resulting composites were characterized by means of typical physicochemical techniques (IR with KBr pellets, PXRD, thermal analysis, ammonia TPD, BET, elemental analysis, SEM). FTIR spectra were recorded using the transmission technique on Bruker Tensor 27 in the range of 400–4000 cm^{-1} with a resolution of 1 cm^{-1}. Usually 1.5 mg of the sample was ground with 200 mg KBr and pressed (150 MPa) to obtain a pellet. Powder X-ray diffraction patterns were recorded on Bruker AXS D8 Advance equipped with Johansson monochromator (αCu Kα1 = 0.15406 nm) in range of $5^\circ < 2\theta < 55^\circ$ with step