

Reconstruction of umbite framework variants by atomistic simulations using XRD and sorption data

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Abstract

The interest in the synthesis of new microporous metal silicates (e.g., umbite) has significantly increased during the last decades, driven by their ability to discriminate molecules based on their size, shape, or polarity. In the present work, different isomorphously substituted Zr-, Sn- and Ti-umbite crystals are reconstructed from powder XRD patterns. Then, the simulated structures are used as input to an algorithm for the determination of adsorption properties of small gas molecules in umbite crystals. In this way, guidance to optimize umbite structures with improved sieving properties can be provided. H₂, NH₃, and CO₂ are examples of gases that are studied here. Our simulations have shown that the cell volume of Ti-umbite is smaller than the corresponding cell volume of Zr-umbite, in agreement with literature experimental data. This observation is fully aligned with our adsorption measurements, according to which Zr-umbite adsorbs considerably larger amounts (40 mg/g) of NH₃, compared to those adsorbed by Ti-umbite at 50 °C (7 mg/g). The same methodology, which involves reconstruction from XRD spectra and sorption simulation, can also be applied to other metal substitutions in the umbite framework.

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1. Introduction

During the last years, there has been an increasing interest in the synthesis of microporous titanasilicates and other mixed octahedral–tetrahedral framework oxides [1]. Among the fruits of the research efforts is the discovery of appropriate conditions for the synthesis of crystals having the framework of the mineral umbite (K₂(Zr_{0.8}Ti_{0.2})Si₃O₉·H₂O), which is found in the Khibiny alkaline massif on Kola peninsula (Russia) and was first described two decades ago [2]. The framework of umbite-type compounds consists of MO₆ (M = Zr, Sn, Ti) octahedra and SiO₄ (or GeO₄) tetrahedra. It was also possible to synthesize different isostructural umbite-materials, like K₂ZrSi₃O₉·H₂O [3,4], K₂TiSi₃O₉·H₂O (AM-2 or STS) [5–7], K₂SnSi₃O₉·H₂O (AV-6)

[8,9] and K₂ZrGe₃O₉·H₂O [10], as well as crystals with different levels of titanium–zirconium [11,12], or tin–zirconium [13] substitution. The K⁺ cations, incorporated in the structure during synthesis, can be exchanged with other cations, and several ion exchanged forms have been investigated in detail [4,5,9,12,14,15]. Notable examples include synthetic Zr-umbite crystals doped with Eu³⁺, which have been tested as optical devices [15], and Sn-umbite structures, which have been tested for the removal of radioactive cations (¹³⁷Cs⁺ and ⁹⁰Sr²⁺) [12].

Their potential for isomorphous framework substitution allows fine-tuning of the properties of umbite materials in order to meet the demands of different applications. For example, Zr-rich silicates with large channels exhibit affinity for Rb and Cs ions, whereas Ti-rich compounds with much smaller channels show preference for K [12].

The small pore size of umbite materials grants them potential for separation of H₂ containing mixtures. Recently [16,17], Sn- and Ti-umbite membranes have been prepared by seeded

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hydrothermal synthesis on porous α - Al_2O_3 and TiO_2 tubular supports. Gas permeation experiments showed that these membranes are able to separate H_2 from N_2 , CO_2 and C_3H_8 , with maximum separation factors of 48, 31 and 47, respectively. The selectivity is attributed to molecular sieving effects; for instance, in contrast to H_2 (kinetic diameter 0.289 nm), N_2 (kinetic diameter 0.364 nm) does not enter the umbite channels (diameter ~ 0.3 nm) and permeates only through intercrystalline defect pores.

The structure of inorganic membranes used in gas separation can be reconstructed at the atomistic level, to study the interaction effect of solute or diffusion molecules with the membrane material. Atomistic simulations of the structure of inorganic membranes (SiO_2 , zeolites) [18–24] have been realized using Molecular Dynamics and Monte Carlo techniques. The reconstruction of inorganic structures at the molecular scale usually includes the following conceptual steps. Initially, the atoms of the membrane materials are positioned at reference bulk lattice sites using literature data. The interatomic potential energy of the configuration is dynamically calculated using some force field description, which relies on either empirical or *ab initio* data. Depending on the available data and the accuracy needed, simple energy descriptions, like the Universal force field (UFF) [25], or more accurate albeit computationally complex force field, like the Compass FF [26], can be utilized for this purpose [27,28]. Boundary conditions are then set, either periodic or of the free surface type. The final step is the total potential energy minimization of the system, using Steepest Descent or Conjugate Gradient techniques, or more advanced techniques, such as the parallel tempering methods [29], and addition of cation or other bulk/surface defects (where appropriate) in an iterative scheme. Using a force field, very useful quantities can be computed, such as momenta, interaction energies, conformational energy barriers, free energies, etc. The atomistic structure is the basis for MD and MC calculations to probe the locations, conformations, and motions of sorbate molecules, in order to reach useful conclusions concerning the actual supply of sorbates to the active sites of membrane structures [27,28].

In the present work, three different isomorphously substituted umbite crystals (Zr, Sn, and Ti) are synthesized and characterized using experimental and simulation techniques. A computational representation of the atomistic structure of the hydrated crystals is derived from powder XRD patterns alone, and is used as input for the theoretical prediction of the dehydrated crystal structure. Furthermore, for the case of dehydrated Zr-umbite crystals, theoretical calculations of the NH_3 adsorption capacity and of the heat of adsorption, based on atomistic Monte Carlo simulations, are compared with the corresponding experimental values as these are appropriately extracted from adsorption and desorption experiments.

2. Experimental

2.1. Synthesis

Isomorphously substituted $\text{K}_2\text{MSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ti, Sn, Zr}$) of umbite crystals were synthesized using the following

molar composition of the gels: $5.46\text{K}_2\text{O} : 3\text{SiO}_2 : 1\text{MO}_2 : 560\text{H}_2\text{O}$ ($\text{M} = \text{Ti, Sn}$) [17] and $10\text{K}_2\text{O} : 3.45\text{SiO}_2 : 1\text{MO}_2 : 311\text{H}_2\text{O}$ ($\text{M} = \text{Zr}$) [13]. The precursor reactants were TiCl_3 solution (15 wt.% TiCl_3 , 10 wt.% HCl , Merck), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98 wt.%, Riedel-de Hën), ZrOCl_2 (30% in HCl , Aldrich), deionized H_2O , KCl (99 wt.%, Merck), KOH (85 wt.%, Merck), and fumed silica (Aerosil 300). The synthesis of Zr-, Sn- and Ti-umbite crystals was performed following the procedure described below. In all three cases, following gel preparation, the hydrothermal synthesis was carried out at 200°C for 48 h.

2.1.1. Zr-umbite preparation

First, a solution was prepared by mixing 1.11 g of Aerosil, and 5.96 g of KOH in 29.45 mL of water. Then, a second solution, containing 3.15 g of ZrOCl_2 mixed in 0.32 mL of water, was added to the first one.

2.1.2. Sn-umbite preparation

Aerosil 300 (0.73 g) was added to a solution of KOH (1.57 g) and KCl (1.33 g) in water (14.71 mL). A clear solution was obtained after 30 min of stirring. A second solution, containing $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (1.36 g) in water (14.71 mL), was also prepared and was kept under stirring for 20 min before mixing with the first one. Upon mixing, a cloudy solution was formed, which was kept under vigorous stirring for another 30 min. Subsequently, 5.58 mL of water were added.

2.1.3. Ti-umbite preparation

Aerosil 300 (0.69 g) was dissolved in a solution of KOH (2.16 g) and KCl (0.49 g) in water (13.86 mL). This solution was then mixed with solution of TiCl_3 (3.69 g) in water (13.86 g). A purple solution was obtained and kept under vigorous stirring for another 30 min before adding the final 5.25 mL of water.

2.2. Characterization

The as-synthesized umbite powders were characterized by scanning electron microscopy (SEM, JEOL JSM-6400) and X-ray diffraction analysis (XRD, Rigaku/Max diffractometer $\text{Cu K}\alpha$ radiation and graphite monochromator). Thermogravimetric analyses (TGA/SDTA851e, Mettler-Toledo, Inc.) have also been used to estimate the amount of water. The TGA experiments were performed in N_2 atmosphere between 47 and 500°C using a heating rate of $5^\circ\text{C}/\text{min}$.

2.3. NH_3 adsorption and temperature programmed desorption (TPD)

NH_3 adsorption experiments were performed on 400 mg powder samples that were placed in a quartz tube, fixed with quartz wool. Each sample was initially degassed, by preheating it at 350°C for 2 h, under flow of nitrogen (200 cm^3 (STP)/min). Adsorption was measured at 50°C using 200 cm^3 (STP)/min of a feed mixture containing 1 wt.% of NH_3 in helium (1% of NH_3 , supplied by Abello-Linde, S.A.). The flow rate of the gas was controlled using a mass flow controller (Brooks 5850 TR series).

The outlet gases were continuously measured by online mass spectrometry (VG ProLab).

The experiments of temperature programmed desorption of NH_3 were carried out using the following procedure. The Zr-umbite crystals were initially placed in a quartz tube and were then equilibrated with a gaseous stream of NH_3 (1% in N_2). After equilibration was reached, the NH_3 flow was switched off, the sample was flushed with Ar while it was simultaneously heated with a constant heating rate. The NH_3 concentration at the exit of the quartz tube was monitored using a mass spectrometer (Omnistar/Pfeiffer Vacuum). NH_3 TPD experiments were carried out at four different heating rates (5, 10, 15 and $20^\circ\text{C}/\text{min}$).

The quantitative analysis of the TPD experiments was performed using the following equation [30,31]:

$$Y = \ln \left[\frac{T_m^2 \theta_m^{n-1}}{(1 - \theta_m)^{n+1} \beta} \right] = \frac{\Delta H}{RT_m} + \ln \left[\frac{VL(\Delta H)}{unAR} \right] \quad (1)$$

where u is the superficial velocity, V the initial amount of adsorbate per unit volume of bed, n the order of adsorption or desorption, R the ideal gas constant, T_m the temperature, θ_m the surface coverage, β the heating rate, ΔH the heat of adsorption, A the ratio of pre-exponential factors of adsorption and desorption rates, and L is the length of the catalyst bed.

The derivation of Eq. (1) [30,31] assumes perfect mixing, free readsorption, coverage and temperature independent heat of adsorption, as well as temperature independent pre-exponential factors for adsorption and desorption.

The TPD curves were fitted using two Gaussian functions. This procedure assumes that adsorption takes place on two energetically different adsorption sites. Each Gaussian curve corresponds to the amount of NH_3 desorbed from a specific adsorption site. For each site and heating rate examined the temperature T_m at which the maximum ammonia concentration is detected is noted, and is used for the calculation of Y , which is plotted as a function of $1/T_m$ (see Eq. (1)). The heat of adsorption for each site is then estimated from the slope of Y versus $1/T_m$.

3. Modeling

3.1. Structure determination

The structure of Zr-, Sn- and Ti-umbite crystals was determined from their X-ray diffraction patterns using as basic computational platform the software Molecular Studio Modeling by Accelrys according to the following procedure.

The X-ray patterns were initially indexed using the ITO method [32]. ITO is a zone-finding method and has been selected because it is well suited for low symmetry systems (orthorhombic and below). According to this method the trial reciprocal lattices are constructed following a two-step procedure. Initially, peaks that might belong to the same plane are grouped. These groups are then combined in order to construct a trial reciprocal lattice. The initial internal symmetries (space groups, systematic absences, number of molecules) were either guessed, or taken from similar literature data [3]. The best positions and conforma-

tions to arrange atoms not belonging to known internal positions were searched in a sequence of minimization of energy methods and “Figure of Merit” analysis, obtained through comparison of the calculated parameters with the experimental data, using established refinement techniques.

More specifically, a combination of Pawley [33] and Rietveld [34] refinement methods was used for the optimum determination of the Zr-umbite structure. To refine the umbite structure, it was necessary to obtain a first approximation of the profile parameters, such as peak profiles, asymmetry parameters, background parameter, line shift parameters, lattice parameters, and a good starting model of the atoms position, as well. The Pawley method was applied for the calculation of these values without having details of the atomic position beforehand, as this tool allowed for the refinement of the intensities of Bragg reflections as freely varying refinement parameters, irrespective of the underlying atomic structure. This method offered the possibility to refine an individual intensity for every expected Bragg peak, allowing for the precise refinement of the cell parameters and for the extraction of a set of structure factor amplitudes. Pawley refinement was applied repetitively, with only a few parameters being refined at a time, up to the point of obtaining a best-valued refinement, in order to find a set of powder diffraction simulation parameters which led to optimum agreement between simulated and experimental data.

Once the initial guesses of the profile parameters were obtained, Rietveld refinement methods were applied to tailor the internal structure of the umbite materials. Profile and lattice parameters obtained from the Pawley refinement method were used for the Bragg intensities calculations in the Rietveld methodology. The sum of all peak contributions produced a calculated powder pattern, which was compared to the observed one, providing a measure of similarity by means of the weighted profile R-factor [34], and the minimum potential energy of the structure as well. This methodology allowed for the concurrent least-squares refinement of profile and structural parameters.

The initial guess of the Zr-umbite structure was taken from data reported previously by Poojary et al. [3], after performing an energy minimization calculation using the Universal force-field [25,27]. More sophisticated forcefields, like the Compass [26,28], could not be used before an optimized version for non-aluminosilicate zeolites is available, so that M–O–Si bonds (M = Zr or Ti or Sn), that exist between the umbite crystal atoms, can be described correctly. However, non-bonded interactions can be described adequately using Compass forcefield, since the (optimized) non-bonded potential description of Zr, Ti, and Sn in relative metal oxides (ZrO_2 , TiO_2 , SnO_2) can be applied.

The initial structures for the Sn- and Ti-umbite crystals have been created by simply replacing the Zr atoms of the refined Zr-umbite structure by Sn and Ti, respectively. The energy of the new structures was initially minimized using the Universal forcefield. For each case, the final structure was determined performing successive Rietveld refinements initially to fragments of the crystal that have been assumed to form motion groups and, finally, to the whole structure. At each successive refinement only one specific motion group was allowed to move and the remaining of the structure has been considered rigid. The

refinements were performed successively in the following nine motion groups: (i) the K^+ cations and the water molecules; (ii) octahedral ZrO_6 ; (iii) one of the tetrahedral SiO_4 ($Si1O_4$); (iv) a second tetrahedral SiO_4 ($Si2O_4$); (v) the last tetrahedral SiO_4 ($Si3O_4$); (vi) zirconium; (vii) all silicon; (viii) oxygen linked to Zr; and finally (ix) oxygen linked to Si. The motion groups mentioned above as well as the order in which refinements were made are not unique. For example, another possible approach is to fit the whole structure first, and then the individual fragments. The above selections of the motion groups as well as the order of the refinements were decided after testing several different groups and sequences. It has been found that the results depend on the selection of the motion group and the order of the refinements, if the initial structure differs significantly from the final one. If the initial (guess) structure is similar to the experimental (final) structure, as was the case of Zr-umbite, then the order of motion group definition is not important. In the case of Sn- or Ti-umbite, however, the initial structures were significantly different from the experimental structures, and the results were strongly dependent on the order in which the motion groups are defined. The optimum structure was selected based on the achieved minimum weighted profile factor (R_{wp}) and minimum energy of the system.

The procedure described above gives information about the structure of the hydrated crystals. In order to compare the theoretical predictions concerning the adsorption of NH_3 with the experimental results it is necessary to use the structure of the dehydrated crystal as input to the methodology that is described in Section 3.2. These structures have been calculated from the ones derived through the refinement method by removing the water molecules and further minimizing the energy of the structure using Universal force field.

3.2. Simulation of adsorption

The hydrated and dehydrated Zr-umbite structure models were imported and used in sorption simulations. The simulations were performed using the Metropolis MC algorithm [35]. The probability ratios of exchange, conformations, rotations, and translation steps were set to 0.4, 0.2, 0.2, and 0.2, respectively. The Compass forcefield was used for the energy description of the interactions during the physisorption of the sorbates, allowing for 10^6 initial time steps (equilibration) and collecting GCMC ensemble data for 10^7 time steps (production). Ewald summation and charge equilibration were used at each step, with the potential energy cut-off radius set at $18.5 \text{ \AA}$, whereas a width of $1 \text{ \AA}$ was used for cubic spline extrapolation to zero (truncation). Two adjacent unit cells were used in each direction ($2 \times 2 \times 2$) for the adsorption calculations. The calculations were performed keeping either the fugacity or the loading constant, while maintaining the temperature fixed at 298 K , which is the temperature at which the XRD spectra and, hence, the structure regeneration, were obtained. The optimized form of NH_3 molecules used employs a pseudo-atom approach for the proper description of the point charges and the dipole moments present in the ammonia molecules.

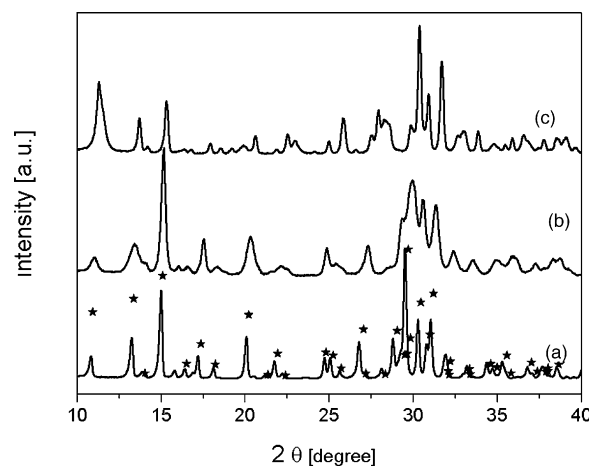


Fig. 1. X-ray powder diffraction patterns for (a) $K_2ZrSi_3O_9 \cdot H_2O$, (b) $K_2SnSi_3O_9 \cdot H_2O$ and (c) $K_2TiSi_3O_9 \cdot H_2O$. The star symbols denote position of the peaks according to literature [2].

4. Results and discussion

4.1. Experimental

Fig. 1 shows the XRD patterns obtained for Zr-, Sn- and Ti-umbite. Following comparison with literature patterns [2], it can be observed that umbite was the only crystalline phase present.

SEM images of as-synthesized Ti-, Sn-, and Zr-umbite crystals are shown in Fig. 2. The morphology of these crystals is similar to that reported in earlier studies [14,17,36]. Despite the fact that all crystals have similar structures, they exhibit different geometry. Zr-umbite consists of bundles of crystals having size $5\text{--}20 \text{ }\mu\text{m}$. Sn-umbite crystals are spherical having uniform size between 1 and $1.5 \text{ }\mu\text{m}$. Ti-umbite crystals have a prismatic shape with uniform size $5 \text{ }\mu\text{m} \times 13 \text{ }\mu\text{m}$. Umbite crystals of various size or morphology have also been reported in the past. For instance, Ti-umbite crystals can be found either as spherical bundles [36] or as prismatic monocrystals [37]. Lin et al. [11] reported that the Zr–Ti molar ratio of the crystals significantly affects their morphology and size. Other titanium silicates, such as ETS-10, show different forms of crystals depending on the reactants used during synthesis [38]. More recently, it has been reported that depending on the support used, the synthesis of Ti-umbite membranes using the same gel compositions and reactives [17] can either induce the formation of aggregates in spherical caps (alumina support) or lead to different morphology (titania support).

The results of the TGA experiments are shown in Fig. 3. The weight loss is higher in Ti-umbite (6.2 wt.%) than the loss in Zr-umbite (4.5%) and Sn-umbite (4.7%) crystals. This result is probably a combination of the difference in the atomic weights of Ti, Zr, and Sn, and the higher content of loosely adsorbed water in Ti-umbite. The weight loss recorded is due to the removal of both physisorbed and bonded water. The relative amounts of the two kinds of adsorbed water can be estimated by using the DTG curve. The amount of water removed until the onset of the DTG peak (Fig. 3b) can be attributed to the physisorbed water. The amount of bonded water has been estimated by subtracting the

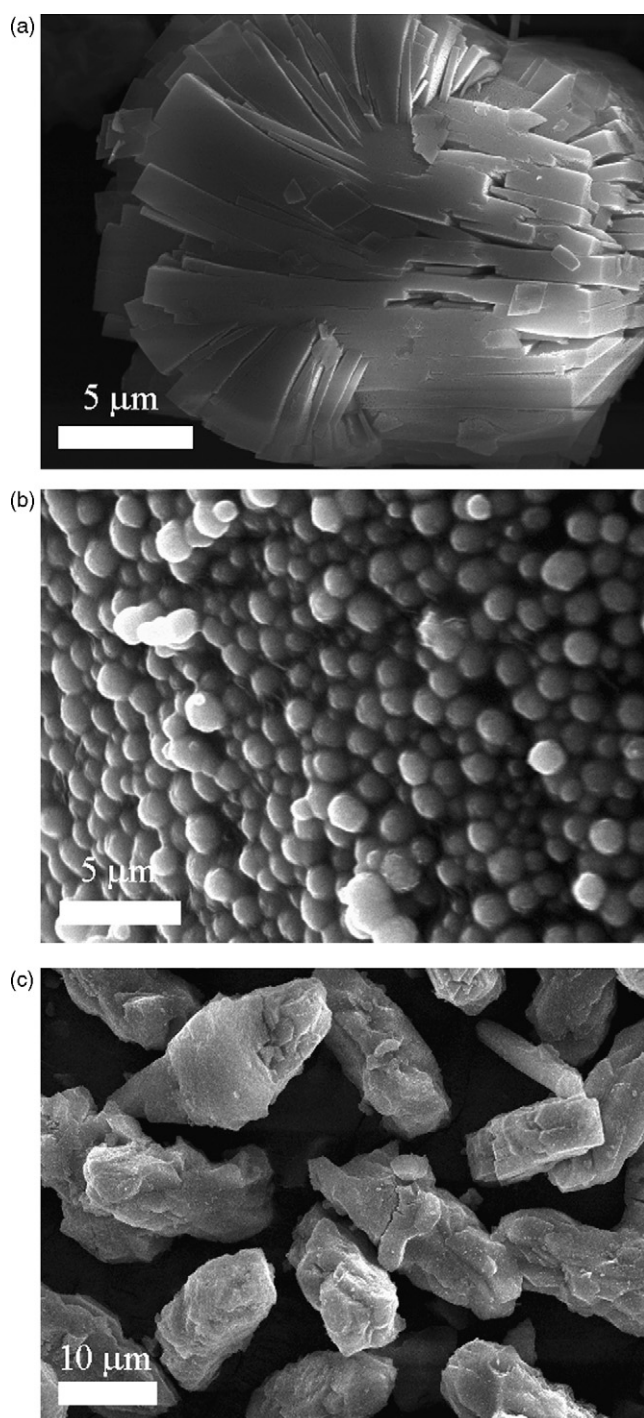


Fig. 2. SEM images of (a) Zr-umbite, (b) Sn-umbite and (c) Ti-umbite crystals.

mass of physisorbed water from the total mass of water removed. The relative amounts of physisorbed and bonded water for each crystal are shown in Table 1. For each crystal the DTG peak has different shape and its maximum is observed at different temperature. Those differences can be attributed either to different binding energy of the water, or to differences in mass transfer rates which result from the dissimilar shapes and sizes of the crystals. The results shown here are within the range reported in the literature. Valtchev et al. [36] reported 7.3 wt.% loss when Ti-umbite was heated between 25 and 450 °C. About 2.16% of

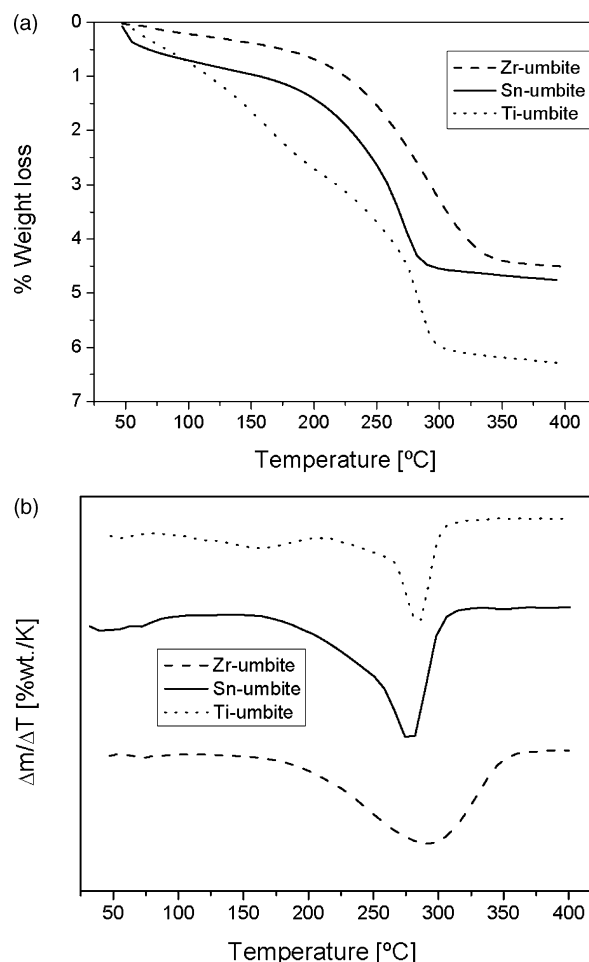


Fig. 3. TGA (a) and DTG (b) analysis of Zr-, Sn- and Ti-umbite crystals.

the weight loss was attributed to water loosely attached, and the rest to strongly bonded water. Other authors [2,7] have reported about 5% total loss weight. This value is close to what is expected based on the molecular formula ($K_2TiSi_3O_9 \cdot H_2O$) of the crystal. The water loss of Ti- and Zr-umbite [11] has also been reported to be about 4.8–5.6 wt.%. Furthermore, most of the water was desorbed between 250 and 400 °C.

The amount of NH_3 adsorbed in each sample of the three different crystals (equilibrated with 1 wt.% NH_3 in helium at 50 °C and 1 atm total pressure) was found to increase in the following order of metal substitution: Ti-umbite (7.1 mg/g) > Sn-umbite (10.4 mg/g), and Zr-umbite (40.7 mg/g). Mixed tin–zirconium silicates have also been synthesized following Ref. [13] in equimolar proportion. It was found that the adsorbed amount (28.1 mg/g) is between the corresponding values for pure Sn- and Zr-umbite.

Table 1
Weight loss (wt.%) derived from TGA-DTG curves for Zr-, Sn- and Ti-umbite crystals

	T_1 (°C)	50– T_1	T_1 –400 °C	50–400 °C
Zr-umbite	187	0.6%	3.9%	4.5%
Sn-umbite	179	1.2%	3.5%	4.7%
Ti-umbite	201	2.8%	3.4%	6.2%

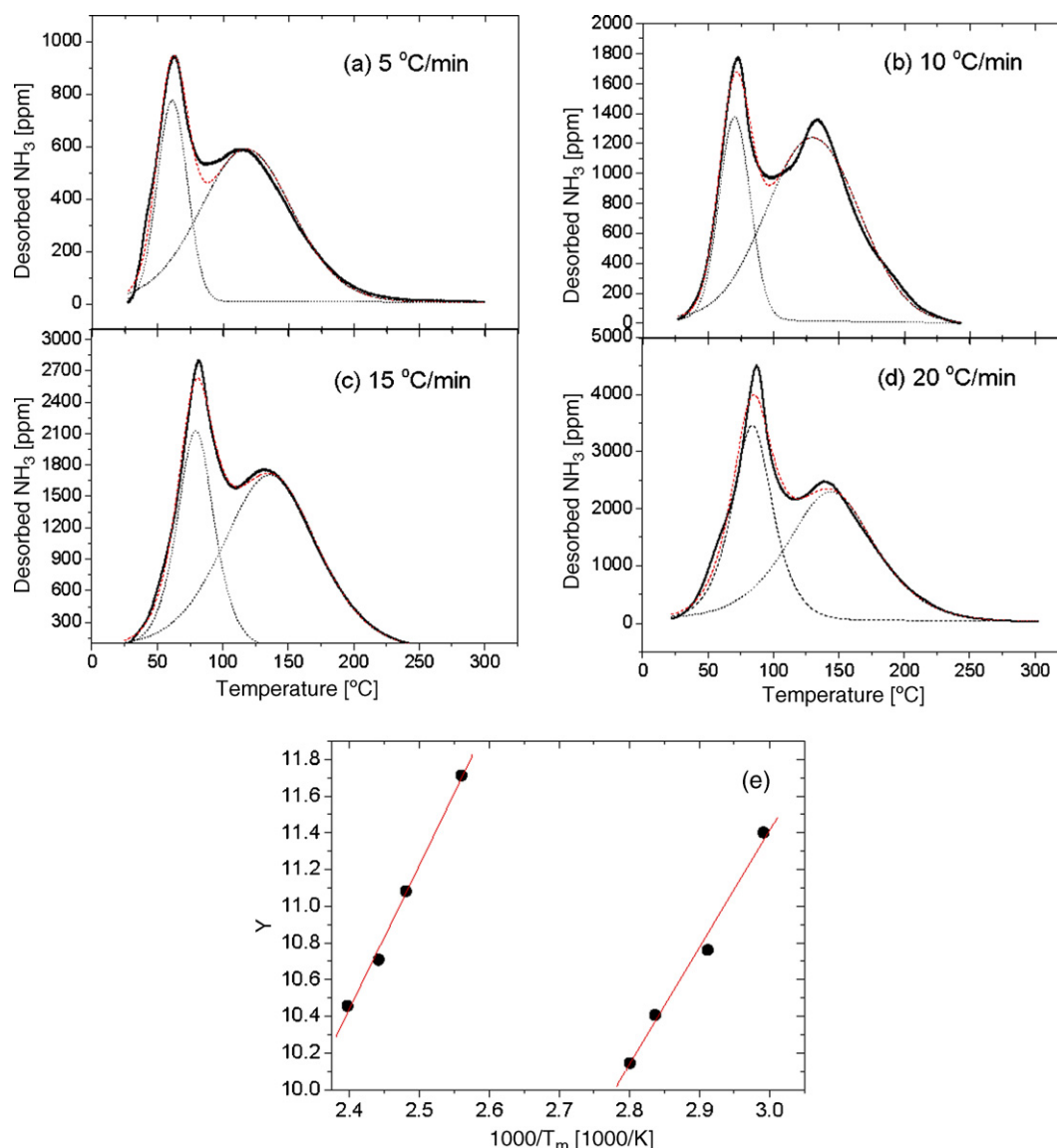


Fig. 4. (a–d) Experimental and fitted NH_3 concentration profiles at the outlet of the quartz cell measured during the TPD experiments. (e) Plot of Y as a function of $1/T_m$ (see Eq. (1)). Heating rates: (a) 5 $^\circ\text{C}/\text{min}$, (b) 10 $^\circ\text{C}/\text{min}$, (c) 15 $^\circ\text{C}/\text{min}$, (d) 20 $^\circ\text{C}/\text{min}$.

The results of the TPD experiments as well as their analysis are shown in Fig. 4 for Zr-umbite crystals. Two characteristic peaks, one in the temperature range 60–90 $^\circ\text{C}$ and one in 100–150 $^\circ\text{C}$, can be observed. The temperature at which the maximum of each peak is observed shifts to higher temperatures as the heating rate increases. The TPD curves were fitted assuming that NH_3 adsorption takes place on two different sites (Fig. 4a–d). Fig. 4e shows the plot of Y (see Eq. (1)) as a function of $1/T_m$. By fitting the points of Fig. 4e, the enthalpy of NH_3 adsorption on the two sites has been found to be 52.9 and 65.5 kJ/mol, respectively.

4.2. Structure determination

Application of the ITO algorithm to the experimental X-ray diffraction spectra reveals that all umbite crystals are orthorhombic belonging to the space group $P2_12_12_1$. This is in agreement with other reports [3,6].

The structures of Zr-, Sn- and Ti-umbite crystals calculated using the procedure described in Section 3.2 are shown in Fig. 5. The refinement converged with R_{wp} at 0.064, 0.066 and 0.139 for Zr-, Sn- and Ti-umbite, respectively. The crystallographic data for all crystals are presented in Table 2. The corresponding fractional atomic coordinates for the hydrated

Table 2
Crystallographic data for hydrated structures

	Zr-umbite	Sn-umbite	Ti-umbite
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a ($\text{\AA}$)	10.3051	10.0909	9.8780
b ($\text{\AA}$)	13.3446	13.1298	12.9082
c ($\text{\AA}$)	7.1973	7.1500	7.1333
V ($\text{\AA}^3$)	989.75	947.31	909.55
R_{wp}	0.064	0.066	0.139

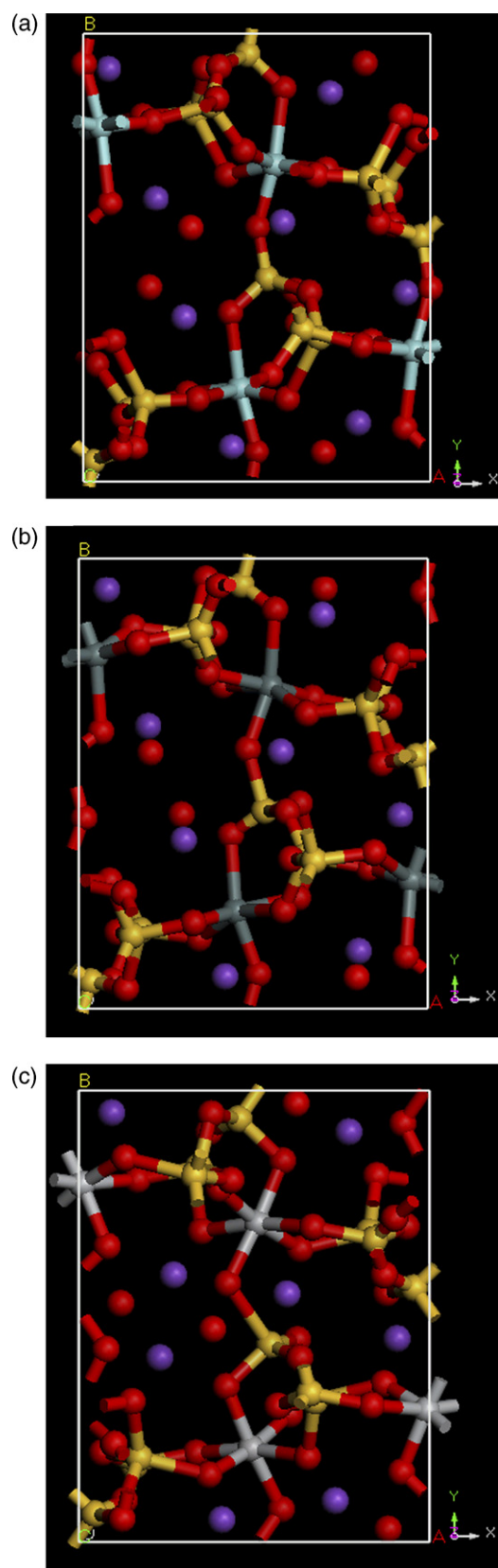


Fig. 5. Ball-and-stick representation of the structure along the z -axis of: (a) Zr-umbite, (b) Sn-umbite, (c) Ti-umbite (atoms rendered at 40% of their vdW radii). Color code: yellow, Si; blue, Zr; dark grey, Sn; light grey, Ti; red, O; purple, K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 3

Fractional atomic coordinates for hydrated Zr-umbite

	x	y	z
Zr1	0.44924 (0.05919)	0.20844 (0.80089)	0.23830 (0.74675)
Si1	0.13253 (0.15198)	0.16020 (0.18389)	0.07152 (0.06043)
Si2	0.02901 (0.03594)	0.04566 (0.06057)	0.75905 (0.75799)
Si3	0.67823 (0.67127)	0.32155 (0.32554)	0.48890 (0.52255)
O1	0.57805 (0.40704)	0.87842 (0.35833)	0.22994 (0.27385)
O2	0.69932 (0.33615)	0.69673 (0.23491)	0.44348 (0.03762)
O3	0.50169 (0.50691)	0.56730 (0.05154)	0.24330 (0.28640)
O4	0.41347 (0.60389)	0.68547 (0.20078)	0.09543 (0.43903)
O5	0.46029 (0.58130)	0.73757 (0.19643)	0.50485 (0.03860)
O6	0.67239 (0.30663)	0.68498 (0.15809)	−0.00578 (0.46197)
O7	0.11761 (0.08339)	0.14700 (0.14266)	0.26977 (0.25238)
O8	0.15179 (0.13563)	0.07718 (0.07241)	0.65030 (0.57222)
O9	0.11051 (0.07017)	0.07423 (0.03871)	0.96760 (0.91263)
K1	0.20985 (0.22125)	0.63209 (0.66523)	0.34845 (0.36285)
K2	0.57429 (0.42840)	0.57806 (0.08382)	0.71526 (0.68889)
Ow	0.19070 (−)	0.43355 (−)	0.38974 (−)

The corresponding values for the dehydrated structure are shown in parentheses and are used in the sorption simulations.

Zr-, Sn- and Ti-umbites are shown in Tables 3–5 in that order. For simplicity, hydrogen atoms of adsorbed water molecules are not shown in Fig. 5 and subsequent ones. Table 3 gives also the fractional atomic coordinates for the dehydrated Zr-umbite, as these are used in the sorption simulations. As seen in Table 2, the unit cell volume decreases in the order of $\text{Zr} > \text{Sn} > \text{Ti}$, which is in agreement with previously reported results [9]. Furthermore, this observation can explain the trend of NH_3 adsorption measurements because the highest amount of NH_3 is adsorbed in the crystal that has the largest unit cell volume.

The structure obtained is formed by MO_6 octahedra ($M = \text{Zr}$, Sn or Ti) which are connected to six SiO_4 tetrahedra (T), and, therefore, do not form $M\text{--O--M}$ bonds. In addition to the $M\text{--O--T}$ bonds, these tetrahedral also form $T\text{--O--T}$ links with each other [6]. This is the most important difference with the zeolite structures which only have $T\text{--O--T}$ type bonds [1]. Some parameters of the umbite structure, such as the size of the rings and the

Table 4

Fractional atomic coordinates for hydrated Sn-umbite

	x	y	z
Sn1	0.45148	0.21574	0.25312
Si1	0.17538	0.17296	0.00321
Si2	0.03287	0.06001	0.72852
Si3	0.65164	0.33851	0.57850
O1	0.43698	0.38475	0.21264
O2	0.34547	0.15500	0.02176
O3	0.51478	0.07645	0.22511
O4	0.58723	0.21722	0.48243
O5	0.62863	0.24494	0.15054
O6	0.32983	0.18940	0.45432
O7	0.10960	0.16924	0.20863
O8	0.09776	0.06207	0.49769
O9	0.13376	0.04442	0.87900
K1	0.19773	0.62705	0.12669
K2	0.42035	0.07071	0.69247
Ow	0.70403	−0.06867	0.44374

Table 5
Fractional atomic coordinates for hydrated Ti-umbite

	<i>x</i>	<i>y</i>	<i>z</i>
Ti1	0.49148	0.20716	0.22529
Si1	0.15840	0.16997	0.05751
Si2	0.54431	0.43715	0.23170
Si3	0.67590	0.31528	0.54296
O1	0.41964	0.34464	0.26988
O2	0.33388	0.19727	0.03979
O3	0.42331	0.57288	0.33700
O4	0.64867	0.19247	0.39956
O5	0.60045	0.28292	0.04807
O6	0.37646	0.14955	0.39661
O7	0.07551	0.19522	0.27002
O8	0.63248	0.41216	0.40479
O9	0.62275	0.44844	0.00217
K1	0.26966	0.59152	0.51571
K2	0.40699	0.04945	0.71767
Ow	0.38133	0.47136	0.67785

bond lengths, are modified when Zr is replaced by Sn or Ti. The umbite structure contains channels in different directions. Channels running along the *c*-axis possess ring openings with 16 atoms, which are formed by four Zr and four Si linked to each other by sharing oxygen atoms [3]. Substitution of Zr with Sn or Ti affects the size of 16-atom ring openings running along the

b- and *c*-axis. The length and width of these rings, projected on the *x*–*y* plane, are shown in Fig. 6a. It is seen that the size ring decreases as the cell volume decreases. However, not all channels decrease in size as the cell volume decreases. For example, the size of another Ti-umbite ring along *c*-axis is larger than that of Sn- and Zr-umbite. This ring is formed by 12 atoms (2Zr, 4Si and 6O) (Fig. 5a). Another important ring having 14 atoms (2Zr, 6Si, and 6O) runs along the [1 1 0] direction; in this case, the major axis of the ring (A) decreases and its minor axis (B) increases, despite the decrease of the volume cell (Fig. 6b). It is interesting to mention that ion diffusion along this ring is blocked by O7.

4.3. Sorption calculations

Four sites of NH₃ adsorption have been identified in the dehydrated structure of Zr-umbite and are shown in Fig. 7. However, the difference in the heat of adsorption between these sites was not found to be significant. In the dehydrated Zr-umbite case, for NH₃ fugacity in the range 1–10 kPa, the average ΔH value was estimated to be 68.2 kJ/mol. This value compares satisfactorily to the experimental ΔH ones (52.9 and 65.5 kJ/mol assuming two active sites). No NH₃ sorption was obtained using the hydrated structure of the Zr-umbite, as expected. In addition, adsorption of NH₃ at 10 kPa and 50 °C has been simulated, and

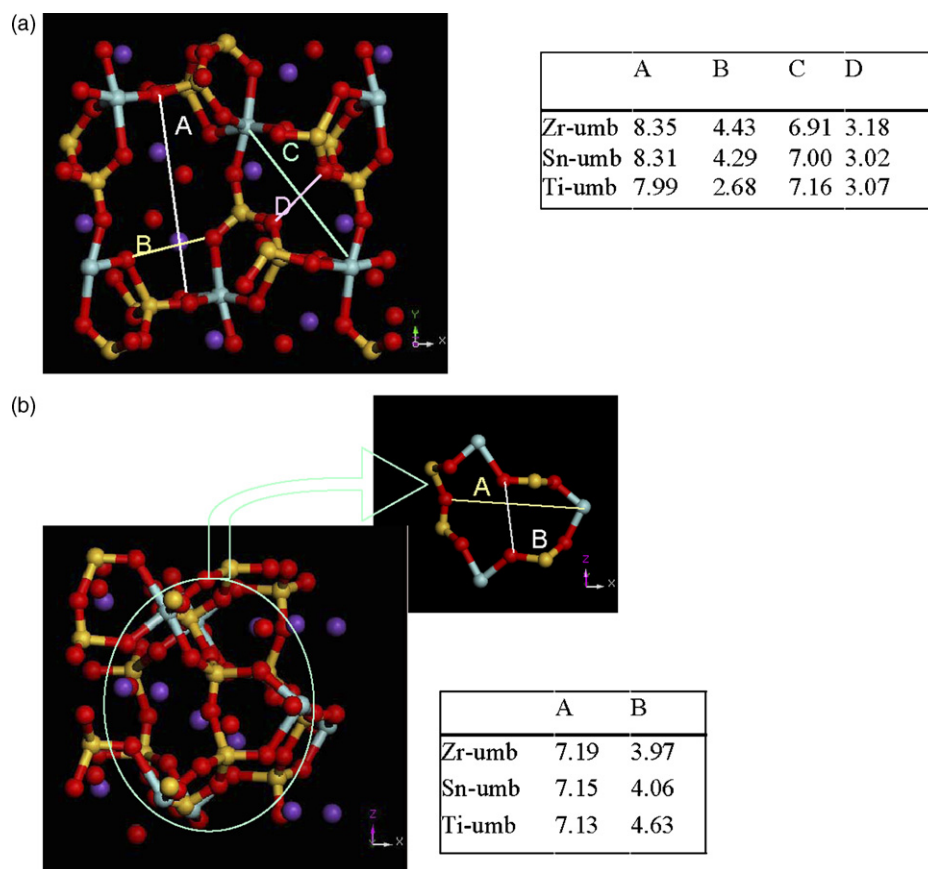


Fig. 6. Size of rings in Å: (a) along *z*-axis projected on *x*–*y* plane; ring with 16 atoms (A and B) and ring with 12 atoms (C and D). (b) Size of ring with 14 atoms projected on *z*–*x* plane. Ball-and-stick representation is used (atoms rendered at 40% of their vdW radii). Color code same as in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

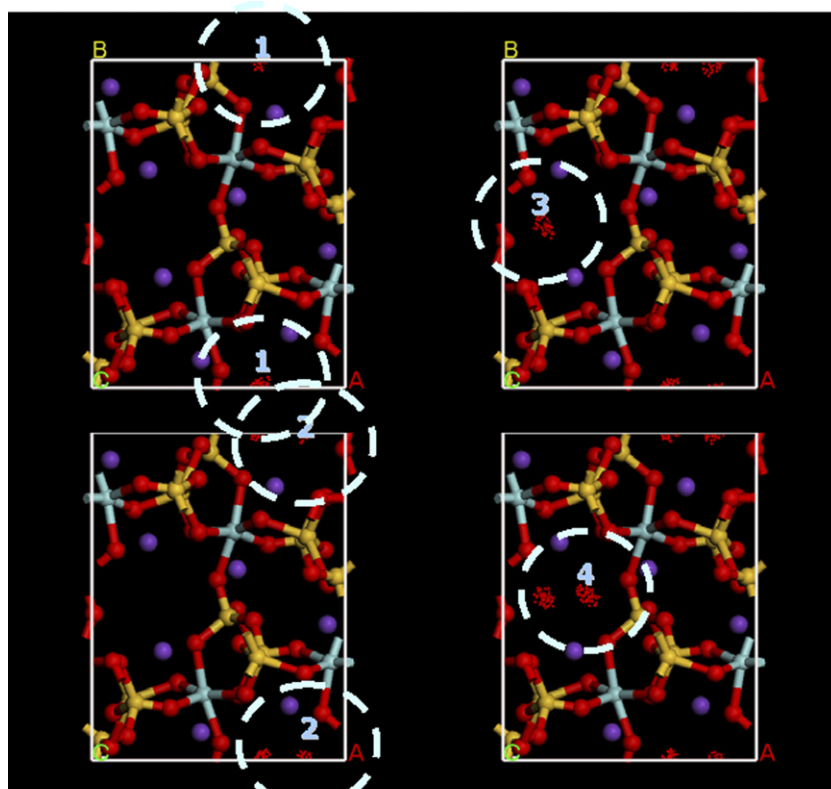


Fig. 7. Ball-and-stick representations of dehydrated Zr-umbite (atoms rendered at 40% of their wdW radii) and cloud-type representation of ammonia sorption sites at decreasing sorption probability (*sp*); the site (1) with the highest *sp* is occupied at loading = 1, the one (4) with the lowest *sp* is occupied at loading = 4. Color code same as in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

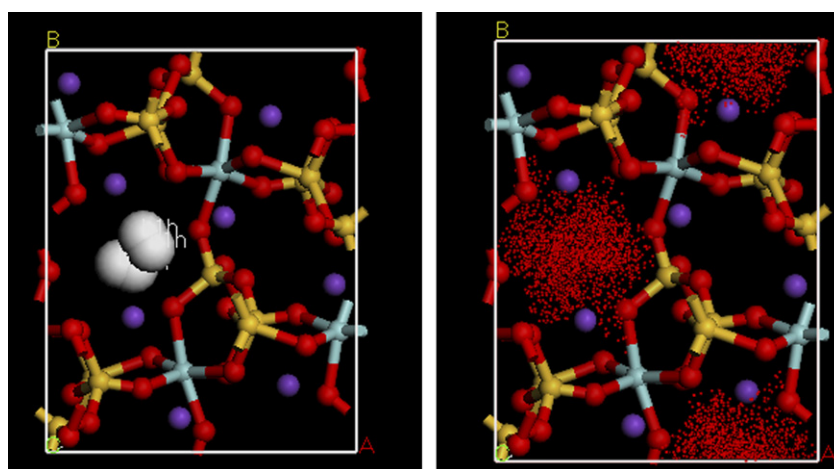


Fig. 8. Hydrogen sorption sites in dehydrated Zr-umbite. Ball-and-stick representation of structure is used (atoms rendered at 40% of their wdW radius). Hydrogen is rendered (a) in sphere-type at 70% of its wdW radius at its most probable (minimum energy) position for molecules loading, $N=2$, and (b) in cloud-type, showing locus of accessible sorption sites. Color code same as in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

resulted in 41.0 mg/g, with is in accord with the experimental value (40.7 mg/g; see above).

Similar simulations of hydrogen sorption on the same Zr-umbite structures (Fig. 8) yielded the heat of adsorption equal to $\Delta H = 3.73$ kJ/mol, which is much lower than the corresponding ammonia value. No CO_2 sorption was obtained using the dehydrated structure of the Zr-umbite. This result is in accord with previous work [17], in which Sn- and Ti-silicate umbite

membranes were able to separate H_2 from CO_2 with maximum separation factors around 31.

5. Conclusions

Computer-aided reconstruction of umbite frameworks at the atomic level was made possible in this work, using XRD-spectra as input data. The Universal force field description appears to

provide more accurate results than more complicated force-fields, like Compass, which require further optimization (bonds) for this type of zeolitic material in order to handle Zr–O–Si, Ti–O–Si, and Sn–O–Si bonds efficiently. However, Compass should be sufficient for transport and sorption calculations (long-range interactions). It is also found that if the initial/guess structure is similar to the experimental/final structure, then the order of motion group definition is not important (Zr-umbite). When the initial structure differs from the experimental structure, the results highly depend on the order of motion group (Sn-, Ti-umbite). Sorption simulation results were obtained using the Metropolis Monte Carlo algorithm for Zr-umbite and were found to be in satisfactory agreement with experimental values.

NH₃ adsorption sites with relatively high ΔH_{ads} (~60 kJ/mol) are expected. Dehydrated structures obtained at higher temperatures are suited for molecular sieving of NH₃. Water was found to prohibit NH₃ adsorption. H₂/CO₂ separation capability of Zr-umbite driven by its internal nanoporous structure is confirmed by the present sorption calculations. The method appears quite suitable for other umbite structures as well. Application of the methodology to Ti- and Sn-umbite crystals is a subject of ongoing work.

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Appendix A. Nomenclature

A	ratio of pre-exponential factors of adsorption and desorption rates
ΔH	heat of adsorption (J/mol)
L	length of the catalyst bed (m)
n	order of adsorption or desorption
R	ideal gas constant (J/mol/K)
T_m	temperature at which the maximum NH ₃ concentration is detected (K)
u	superficial velocity (m/s)
V	initial amount of adsorbate per unit volume of bed (mol/m ³)
β	heating rate (°C/min)
θ_m	surface coverage when the maximum NH ₃ concentration is detected

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