



Organosilanes functionalization of alumino-silica zeolites for water adsorption applications



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ABSTRACT

Standard zeolites 4A and 13X have been synthesized and modified by reaction with dimethoxydimethyl silane, propyltrimethoxy silane, octyltrimethoxy silane and octadecyltrimethoxy silane, respectively. The modified zeolites were analyzed by X-Ray diffractometry, FTIR spectrometry and water adsorption measurements. Results showed that silane molecules bonded to the external surface of zeolite particles with no chance of entering the zeolite porosity. Only “short-chain” silanes dimethoxydimethyl and propyltrimethoxy grafting demonstrated having an influence on the hydrophilic behavior of the modified zeolites. The main effect was a shift of the adsorption isotherms in the low partial pressure range towards a more hydrophobic trend, which represents an interesting result for adsorption application when low temperature regenerations are required.

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1. Introduction

Since the first studies on vapors adsorption on solid porous materials for heat pumping applications the research activity focused on the zeolite/water pair as the most simple and profitable combination of adsorbent material/vapor for the outstanding characteristics of the two components [1]. If water continues to be the most promising cryogenic fluid for its known thermophysical properties and incomparable environment compatibility, zeolites have been progressively put aside for their “excessive” water affinity. Commercial zeolites, indeed, rarely show adsorbing properties perfectly suitable to heat pumping use, the main drawback being the need of a high temperature heat source to desorb the vapor out of the material pores allowing the thermodynamic cycle of the heat pump to continue [2–4]. In the last years, new adsorption materials have been successfully proposed, like zeotype AlPOs and SAPOs, for their low hydrophilic character, high water capacity and high adsorption/desorption enthalpy [5,6]. All these characteristics, indeed, have promoted the use of SAPOs in adsorption heat pumps driven by low temperature heat sources, like low temperature waste heat, solar cells, industrial and civil exhaust combustion gases [5]. However, the scarce commercial

availability and the relatively high cost and low hydrothermal stability are important drawbacks that restrict the industrial implementation of SAPOs [6]. Alumino-silica zeolites, on the other hand, are easily accessible, low cost and largely employed catalytic and adsorbent materials. During the years, several attempts to adapt adsorption performances of zeolite 4A, X and Y to the characteristics of adsorption chillers and heat pumps have been done. The principal methods are based on the modification of the zeolite porosity by ion exchange [7] and/or by variation of the zeolite Si/Al ratio by specific treatments like de-alumination [6,8]. The results, however, showed that a significant reduction of the high water affinity was only obtained at the expense of the original water sorption capacity.

In this work, typical alumino-silica zeolites 4A and X have been treated with solutions of different silane agents with the purpose of modifying their adsorption properties towards a more hydrophobic behavior. The first studies on zeolites modification by silane compounds date back to the early seventies when the focus was the modification of the zeolites selectivity and catalytic activity [9]. More recently, several silanes have been used as coupling agents for zeolite mixed membranes for gas separation [10,11] or binders for the deposition of zeolite coatings on metal surfaces for sensors [12,13], corrosion protection [14] and adsorption technologies [15]. In our case, it was observed that the grafting of dimethoxydimethyl silane on the surface of zeolite 4A particles and propyltrimethoxy silane on zeolite X interfered with the adsorption of the water

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molecules at very low partial pressure, causing the pores to begin to fill at higher vapor pressures, as shown by gravimetric measurements of the adsorption isotherms. Such a behavior can be interpreted as a reduction of the original water affinity.

2. Experimental

Sodium form of zeolite 4A (LTA, Si/Al = 1) and X (FAU, Si/Al = 1.5) have been synthesized by standard hydrothermal synthesis according to the formula reported in Ref. [16].

Four different silane compounds have been used for the preparation of the modified zeolite 4A and X: dimethoxydimethyl silane (Aldrich, 95.0%), propyltrimethoxy silane (Aldrich, 97%), octyltrimethoxy silane (Aldrich, 96%), octadecyltrimethoxy silane (Aldrich, 90%). In a typical synthesis the silane compound is hydrolyzed in a solution containing ethanol (90% vol.), distilled water (5% vol.) and silane (5% vol.) The solution pH is adjusted at 4.2 by acetic acid addition to hinder the monomers self-condensation [17–19]. Finally, the silane solution is aged for 24 h at room temperature under stirring. Part of such a silane solution (around 70% wt.) is mixed with the synthesized zeolite powder (around 30% wt.) in order to maintain the weight ratio between zeolite and silanes fixed at 85/15 (% wt). The mixture is, then, homogenized in an ultrasonic bath for 15 min and left to age for 24 h at 25 °C under gentle agitation. Finally, the powder is filtered, washed with distilled water and dried in an oven at 80 °C overnight.

Both zeolites have been tested with all silane compounds, as shown in Table 1.

All porous materials, pristine and modified zeolites, have been characterized by X-Ray diffractometry (Bruker D-8 Advance, CuK α , 40 kV–40 mA), FTIR spectroscopy (Agilent Cary 670 FTIR) and adsorption measurements by vacuum microbalance (Surface Measurements Systems DVS Vacuum). Infrared transmission spectrometry was carried out on wafers of powder samples mixed with KBr, from 400 to 4000 cm⁻¹. Water adsorption isotherms were measured at T = 25 °C on powdered samples of 20 mg with a precision of 0.1 μ g on the measured weight. The samples, before water adsorption, were activated (degassed) at 300 °C in vacuum (P = 133 Pa) for 3 h. Each adsorption isotherm presented in the following was obtained as an average of three measures on three different samples of the same material. The error among the measured isotherms was less than 1%.

Thermal stability of modified zeolites have been studied by TGA analysis (TA Instruments Q600-STD) from 30 to 350 °C with an heating rate of 5 °C min⁻¹, under a constant flow of nitrogen.

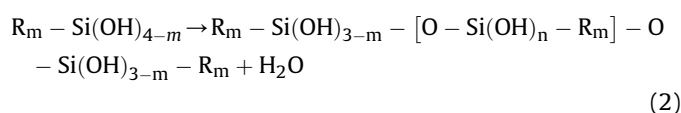
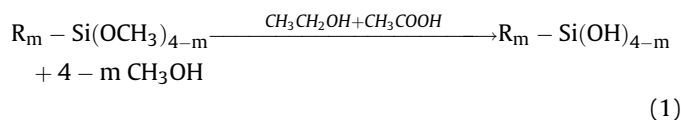
3. Results and discussion

In Fig. 1, X-Ray diffractograms and water adsorption isotherms of the original zeolites synthesized according to [16] are shown. Both characterizations (Fig. 1a and b) confirm the formation of pure, 100% crystalline, zeolite 4A and zeolite X [20,21]. Water adsorption isotherms of Fig. 1b, in particular, show the typical trend of aluminosilica zeolites corresponding to Type I isotherm [22], where high water uptake values are reached from the very low partial pressures. In high hydrophilic zeolites like zeolite 4A and X,

water adsorption begins filling the smallest β cages of the aluminosilica framework at very low partial pressure [23–26]. Increasing partial pressure, water molecules continue diffusing through the zeolite pores filling the largest cages (α cages in LTA and supercages in FAU). Such behavior is evidenced in the adsorption isotherms by a discontinuous increase of the water uptake curve (Fig. 2) and is also confirmed by the values of the differential adsorption heat measured at low P/P₀ ($\Delta h = 120$ –90 kJ/mol) and high P/P₀ ($\Delta h = 60$ –70 kJ/mol) [20,24]. At low pressure, indeed, the water–zeolite interactions dominate while at high pressure, once the pores are partially filled, the water–water interactions become more important [23].

After reaction with silanes, X-Ray diffractograms of both modified zeolites 4A and X (here not reported for brevity) did not show significant differences with the pristine zeolites, demonstrating that no structural modifications of the original zeolite frameworks were induced by the silane treatments.

Alkoxysilanes hydrolyze in ethanol to give the corresponding silanols (1), which partially condense to siloxanes (2). Both reaction rates are strongly dependent on pH, however, in an acidic environment the condensation reactions are significantly slowed down [17–19].



m = 1,2

Silanols condense with hydroxyl groups on the zeolite surfaces according to the scheme in Fig. 3. Terminal hydroxyl groups are always present at the zeolite crystals surface due to the bonding terminations of the zeolite lattice and/or cations deficiency [20,27]. As shown in Fig. 3, complete bonding to the zeolite surface of trialkoxysilane and dialkoxysilane is unlikely for steric reason. The remaining silanol groups can condense with other hydrolyzed silanes or stay in free form.

The possibility for the silanes used in this study to diffuse into the β cages of zeolite 4A and X is excluded for steric reasons: the smallest silane used, S2, has a molecular diameter (estimated on the basis of the Connolly molecular surface) of ≈ 4 Å, which is too large for the narrow β cage windows (≈ 2.2 Å) or even for the α cages (window size = 4.2 Å) of zeolite 4A. In zeolite X, the largest 12-T ring windows of the FAU structure have size = 7.35 Å so that, theoretically, silanes could enter [28]. In solution, however, the zeolite supercages are filled with water clusters electrostatically bonded to Na⁺ cations that will not be shifted by the silane molecules whose dipole moment is significantly lower.

From this point of view, the IR characterization has partially confirmed the silanes chemisorption on the zeolite crystals surface, because of the difficulty to detect the smallest silanes S2 and S3. For

Table 1
The zeolite/silane samples prepared.

Sample	Silane molecule	Zeolite/silane [% wt]
4A- -X	-ZS2 (CH ₃) ₂ -Si(OCH ₃) ₂	Dimethoxydimethyl silane S2 85/15
	-ZS3 C ₃ H ₇ -Si(OCH ₃) ₃	Propyltrimethoxy silane S3 85/15
	-ZS8 C ₈ H ₁₇ -Si(OCH ₃) ₃	Octyltrimethoxy silane S8 85/15
	-ZS18 C ₁₈ H ₃₇ -Si(OCH ₃) ₃	Octadecyltrimethoxy silane S18 85/15

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