



Acidity and basicity of zeolites: A fundamental approach[☆]



Guido Busca

Dipartimento di Ingegneria Civile, Chimica e Ambientale (DICCA), Università degli Studi di Genova, P. J.F. Kennedy, 1 16129, Genova, Italy

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ABSTRACT

The main data concerning acidity and basicity characterization of protonic and cationic zeolites are described and discussed. In particular, experimental data concerning IR studies of the adsorption of pyridine, CO and CO₂ on Na-zeolites (Na-X, Na-A, Na-MOR) and on protonic zeolites (with emphasis on H-Y and USY) are described and discussed. The nature of the Lewis acid and basic sites as well as of the Brønsted acid sites is discussed with a fundamental chemical approach.

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1. Introduction

Protonic zeolites represent today the most prominent class of environmentally friendly solid acid catalysts, largely used in industry for catalytic cracking, alkylations, skeletal isomerizations, etc. [1–5]. Some transition metal-containing zeolites find application as redox catalysts, such as for catalytic reduction of NO_x with ammonia [6,7] and for the abatement of N₂O by decomposition [7,8] and reduction with methane [8]. Alkali and alkali earth cationic zeolites are largely used as industrial adsorbents for gas purification [9] including CO₂ capture [10], to produce membranes for gas separations [11], and as ion exchangers for water softening [12]. The possible application of cationic zeolites as “basic catalysts” is mentioned [13,14] but actual industrial applications seem to be still absent [15,16]. The discovery and application of zeolites has been strictly linked with the development of refinery and petrochemistry, but these materials will have a key role also in the re-starting era of chemistry based on biomass conversion [17].

In most of their applications, acidity and basicity of zeolites are key properties. In spite of this very relevant practical role, still a lot of questions are open concerning the behavior of zeolites, in particular as acid and basic materials.

In this paper, the acido-basic properties of zeolites are reconsidered, based on spectroscopic measurements and on the known catalytic and adsorption behavior, with a fundamental chemical approach.

2. Materials and experimental methods

Data on the materials used in the experiments reported in the paper are reported in Table 1. Fourier Transform InfraRed (FTIR) spectra were recorded using Nicolet 380 FT-IR spectrometers. Adsorption/desorption studies were performed using the pure powders pressed into thin wafers and activated in the IR cell, connected with a conventional outgassing/gas-manipulation apparatus. Activation was performed by heating under vacuum (10^{-3} – 10^{-5} Torr) at 773 K. The activated samples were contacted with vapour/gases (water, pyridine and CO₂) at room temperature (r.t.) for 15 min; later, the IR spectra of the surface species were collected in continuous evacuation at room and increasing temperatures. CO adsorption was performed at 130 K (real sample temperature measured by a thermocouple, when the external reservoir of the cell is full of liquid nitrogen) by the introduction of gaseous CO (30 torr) inside the liquid nitrogen cooled low temperature infrared cell containing the previously activated wafers. IR spectra were collected under evacuation upon warming at increasing temperatures between 130 and 273 K, as the result of the progressive decrease of the level of liquid nitrogen in the cell reservoir.

[☆] Based on the lecture given at the IZC18 Preconference School in Campinas (Brazil), June 2016.

E-mail address: Guido.Busca@unige.it.

Table 1
Materials under study.

Material	Producer/provider	Si/Al ratio	Na ₂ O % wt
Na-X	Grace Sylobead MS C 544	1.2	21.8
Na-X	Laboratory	1.3	nd
Na-MOR	Zeolyst CBV 10A	6.5	6.6
Na-LTA	Fluka	1	nd
H-FER	Zeolyst CP 914C ^a	10	0.05
H-MFI 30	Zeolyst ^a	15	nd
H-MFI 50	Zeolyst CBV 5524G ^a	25	0.05
H-MFI 280	Zeolyst CBV 28014 ^a	140	0.05
H-MWW	Laboratory	15	nd
H-BEA	ENI	50	nd
H-BEA	Zeolyst CP 814E ^a	12.5	0.05
H-MOR (10)	Zeolyst CBV 21A ^a	10	0.08
H-MOR (10)	Süd Chemie	10	nd
H-MOR (45)	Süd Chemie	45	nd
USY	Zeolyst CBV 720	30	0.03
HY	Zeolyst CBV 400	5.1	2.8
ReY	Grace	2.7	RE ₂ O ₃ 12.2%

^a Originally are ammonium forms.

3. Acido-basicity of cationic zeolites: the case of on Na-zeolites

3.1. Structural chemistry of cationic zeolites

Zeolite's structure can be viewed as derived from a microporous silica polymorph, such as a "silicalite". The substitution of aluminum for silicon in a silica covalent framework leads to a charge un-balance which must be compensated by "extra-framework" cations, mostly alkaline. This occurs also for non-zeolitic systems such as in the cases of the so-called "stuffed silicas". Stuffed silicas are alkali aluminosilicates with structures strictly related to the crystalline forms of silica, but with Al ions substituting for Si in the framework and alkali cations in the interstices to counterbalance the resulting charge defect. This is the case, for example, of β -eucryptite (LiAlSiO₄, a stuffed β -quartz), where Li⁺ ions enter "extra-framework" tetrahedral interstices of the quartz framework, or nepheline (NaAlSiO₄, a stuffed tridymite) where the larger Na⁺ ions enter extra-framework octahedral interstices of the tridymite structure. Interestingly, these solids have ion-exchange capacity [18,19]. A similar mechanism also occurs in the amorphous networks of silicoaluminate glasses [20].

In the case of natural and "cationic" zeolites, the balancing cations (usually alkali or alkali earth ions) are located in relatively large cavities formed by the [Si_{1-x}Al_xO₂]^{x-} negatively charged framework, where $x \leq 0.5$, which means that the Si/Al atomic ratio never is lower than 1 (Lowensteins' rule [21]). The cations are exchangeable, thus zeolites may also act as cationic exchangers. The exchange can be performed with ammonium ions which can be later decomposed into gaseous ammonia and a proton. This allows to produce protonic zeolites, which are very strong solid Brønsted acids. Today, protonic zeolites are mostly synthesized directly, by using templating agents. In this case the protons may be residual from the combustion or decomposition of the templating agents.

3.2. Faujaste Na-X and zeolite Na-LTA: zeolitic sodium, aluminum orthosilicates

Sodium zeolites are denoted by the formula Na_xSi_{1-x}Al_xO₂, where $x \leq 0.5$. In the case of faujaste Na-LSX (Low Silica X) and zeolite Na-LTA, $x \sim 0.5$, i.e. Si/Al atomic ratio is ~ 1 , thus the formula is NaSiAlO₄. This makes these zeolites polymorphic forms of nepheline, a stuffed derivative of tridymite, and carnegierite, a stuffed derivative of cristobalite, all characterized by the formula

NaSiAlO₄. As also in the case of nepheline and carnegierite, Si and Al essentially regularly alternate in the tetrahedral-based framework, thus producing sodium, aluminum orthosilicates: orthosilicate anions are formed, whose oxygen atoms are ionically bonded to one tetrahedrally coordinated Al³⁺ cation each and to at least one Na⁺ ion each.

The ideal faujasite structure (Fig. 1) is formed by wide supercages (13 Å diameter) accessed through 12-member silicate rings (12MR) with 7.4 Å diameter, much smaller sodalite cages accessed through 6-member silicate rings (6MR) and hexagonal prisms connecting the sodalite cages. The stoichiometry of the unit cell of a Na-LSX zeolite is Na₉₆[Al₉₆Si₉₆O₃₈₄], containing 8 sodalite cages, 8 supercages and 16 hexagonal prisms. Four crystallographically different oxygen atoms exist in the structure (Fig. 1), two of which (1 and 4) point into the supercage, one (2) into the sodalite cage, and the fourth (3) into the hexagonal prism. Several possible extraframework cationic positions may be occupied [22,23]. In dry faujasites, Na⁺ cations sit on different sites called site I (with the alternative of site I'), site II, and site III (with the alternatives of site III'a and III'b [24]). Site I is in the center of the hexagonal prism (16 per unit cell) while the alternative sites I' are just over of the 6MR in the sodalite cage (32 per unit cell). Site II (32 per unit cell) is just above the center of the 6MR separating supercages and sodalite cages. Site III (48 per unit cell) is just above the 4MR separating supercages and sodalite cages, but has alternatives in sites III', III'a and III'b, in near positions off center the 4MR [24].

A theoretical perfect Na-LSX zeolite, with Si/Al ratio = 1, has full occupation of sites I and II, and essentially half occupation of sites III, with no occupation of sites I', III'a and III'b. In the case of Na-X zeolite, with Si/Al ratio 1.2–2, occupancy of sites I is < 1, with some occupancy of sites I', occupation of site II is still essentially full, while occupancy of sites III is low, the alternative sites III'a and III'b being mainly occupied. Due to the small size of the windows, most authors (except few [25]) suppose that sodalite cages and hexagonal prisms, where sites I and I' are located, are inaccessible to polyatomic molecules. Thus, all the adsorption and catalysis chemistry of faujasites would occur in the supercages. These large cavities contain (in the real Na-X structure) in average a little less than 10 Na⁺ ions, 4 of which are located at site II and a little less than 6 located in sites III'a and III'b. Na⁺ ions in sites II are bound to three O(2) oxygen atoms of the 6MR, those in site III'a are only coordinated to one O (4), but interacts also with two O (1) atoms, those in site III'b interact only with two O (4) and one O (3) oxygen atom. Thus, these Na⁺ ions have very low overall coordination with quite weak coordination bonds, and may also be influenced by their mutual electrostatic repulsion.

Zeolites denoted with the LTA code (Linde Type A, Fig. 2) are small pore zeolites characterized by a cubic structure. The sodium form is another NaSiAlO₄ polymorph. Also in this case, the stoichiometry of the "perfect" unit cell is Na₉₆[Al₉₆Si₉₆O₃₈₄], containing 8 α cages (or supercages), and 8 β cages (sodalite cages). The sodium ions occupy three main sites [26], referred to as site I, II and III, all located nearly at the external surface of the supercages. Sites I, fully occupied, are located at the centers of the 6MRs separating sodalite cages from supercages, with a very small displacement away from the plane of the ring toward the sodalite-cage. Sites II are located at sites associated with the 8MRs separating supercages each other, in the plane of the ring but offset from the ring center, interacting with three oxygen atoms in the ring. Sites II are nearly half occupied, with nearly one Na atom per 8MR. The occupancy of site III, located above the center of the 4MRs, is 5–8%, random. In average, the supercages, that have a diameter of near 11.5 Å, contain 12 Na⁺ atoms. Thus the supercages of zeolite Na-LTA are smaller but contain more sodium ions than the supercages of zeolite Na-X.

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