EXPERIENCE IN ANALYZING VIBRATIONAL SPECTRA OF SOLIDS AND SOLID-SOLID INTERACTIONS

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Abstract

The theoretical analysis of vibrational spectra of solid and solid-solid interactions is critically reviewed and analyzed.

Keywords: Zeolites, solid-solid interactions, vibrational spectra

Introduction

As an example concerning the vibrational spectra of solids and solid-solid interactions, coverage with solid layer or layers of multivalent metal species in zeolites is analyzed. In order to overcome disparity in interpretations concerning the number as well as the apparent frequency values of bands, the vibrational spectra of the following components in loaded Zeolites are to be considered separately.

1. Zeolite substrate (adsorbent),
2. Monolayer and Multilayer coverage (adsorbate),
3. Solid-solid interaction products,

Moreover, surface modes of items 1 to 3 have to be taken into account.

In addition to shifts of non-degenerate bands and to splittings of degenerate bands (site group effect), correlation field splittings (factor group effect), will be also operating. Site group effect is a measure of the influence which the surroundings lattice, in its equilibrium configuration exerts on each componenet. Correlation field effects are due to interactions with internal vibrations of other molecules in the same unit cell of the crystal. Both degenerate and nondegenerate internal vibrations may split, since the potential energy will differ as internal vibrations can be either in-phase, or partly out of phase in the unit cell. One fundamental vibration can be split up to m bands where m is the number of molecules in the smallest volume, or primitive unit cell. In addition to both site group and correlation field effects especially affecting asymmetric type bands, and in addition to long range longitudinal-transverse splittings, different mixed modes and short range forces causing different frequencies for different crystal directions, together with optical surface modes[1] are more or less expected. Optical surface modes which can be considered as localized vibrations at the surface (with an

exponentially decreasing amplitude perpendicular to the surface) and which can be described by a wave vector parallel to the surface. Additional surface modes may also be present that arise from surface imperfection and adsorbed atoms or microscopic layers of impurities (like water vapour content). Zeolite itself is also never one hundred percent crystalline and can suffer crystal imperfections like cracks and holes. Disordered and defect crystals can thereby introduce additional fundamentals that can be very large in number as local effects occur due to specific defects. Of course, the resolution may not be complete either because of low magnitude of splitting or due to band broadness, overlapping with neighbouring bands or with other components or interaction products bands or because of low intensity of one of the splitted bands. The above mentioned effects may be specially pronounced with increasing temperature. On the other hand, Surface imperfection such as cracks and holes which serve to increase surface area per unit mass greatly over the apparent geometrical dimensions are expected to diminish for understandable reasons, with progressive calcination and temperature elevation. As mentioned above, these effects are expected to be reflected in asymmetric shape of bands and in variation in intensity as well as in multiplicity changes of bands. On the other hand, spectral variation as a function of framework structure will be less pronounced in symmetric bands because symmetric bands with low dipole moments are less influenced by interactions with internal vibrations of other molecules in the crystal. Differences in the vibrational spectra can also occur due to other special features for each solid component as in case of different Si/Al ratio controlling pore opening of respected zeolite, and/or different deposition procedures and hence concentration of adsorbate, and/or as eventual solid-solid interaction products may be present.

As for pore opening, they are responsible for diffusion of adsorbate and accordingly responsible for physical adsorption forces. They must therefore be taken into account because they result in formation of different semi-crystalline, defect crystallites or amorphous aggregates (XRD) with different geometry and different crystalline orientation and aggregate dispersion, each will have its own characteristic vibrational spectrum. Specific effects of different deposition procedures on solid-solid interactions, will be discussed in paragraph III.

Zeolite Structure

The primary building units of zeolites[2] are $[SiO_4]^{4-}$ and $(AlO_4)^{5-}$ tetrahedra linked together by corner-sharing, forming bent oxygen bridges. Many Zeolites structures

are based on secondary building unit that consists of 24 silica or alumina tetrahedra linked together where 4- and 6- rings are linked together to form the sodalite unit (or ß- cage). The mineral sodalite itself is composed of these units, with each 4- ring shared by two ß -cages in a primitive packed array forming cavities; theses cavities are linked together to form channels which run parallel to all three cubic crystal axes. The sodalite units in faujasite are linked by oxygen bridges between four of the eight 6-rings in tetrahedral array forming hexagonal prisms. The synthetic zeolites X and Y also have this basic underlining structure. Zeolite X structures have a Si/Al ratio between 1 and 1.5, whereas zeolite-Y structure have Si/Al ratio between 1.5 and 3 ratio. The tetrahedral array encloses a large supercase (α-cage) which is entered through a 12-ring window. The naturally occurring zeolite mineral mordenite has a Si/Al ratio of 5.5 and ZSM can have a Si/Al ratio between 20 and ∞ (the latter being virtually pure SiO_2).

The Si/Al ratio affects the width of cavities and controls the diameter of pore-openings (windows) in sofar as the unipositive cations, which preserves overall electrical neutrality (which AlO_4 tetrahedron needs), and which are coordinated to water molecule and thus occupying a considerable volume, can only be accommodated by forming cavities in the silicate lattice and form tunnels that run entirely through the solid.

Thus the most important structural features of zeolites are the network of linked cavities or pores forming a system of channels throughout the structure. A controlling factor for admittance inside the cavities is the size of window or pore-opening into the channels, hence the number of tetrahedra forming the window. Faujastic for example has a 12-ring window of diamter 740 pm, leading into the α -cage of diameter 1180 pm. Zeolites have large internal surface areas and high sorption capacities for molecules small enough to pass through the window into the cavities. Zeolites are expected to be able to absorb and strongly retain molecules just small enough to enter cavities and channels.

Specific Surface Solid-solid interactions

As stated in the introduction, different methods of zeolite solid layer or layers coverage (impregnation or vapour deposition) using multivalent metal species are expected to result in formation of surface layers possessing variable crystallites, therefore acquiring different shape and structure. Crystallinity of the respective zeolite will be perturbed and gradually become unstable as a result of eventual solid-solid interaction. Liquid deposition procedure predominally impregnate outer zeolite

surface, resulting in outer surface loading of the zeolite since oxoanionic or neutral adsorbate species will penetrate only with difficulty through zeolite windows in presence of water. On the other hand vapour deposition causes more loss in crystallinity because better homogenous dispersion is more feasible using vapour deposition resulting in substantially more loss in crystallinity and surface area of the respective zeolite.

As stated above, beside the variables of different deposition procedures, different concentration of the adsorbate, different Si/Al ratio controlling window dimension, thus affecting the physical and chemical affinity of the respective zeolite; temperature elevation whose rise is expected to affect considerably the rate of diffusion and hence, size and shape and consequently reactivity of the surface interacting components, a controlling factor in latter to be discussed chemisorption. Additionally, changes are expected to occur between the surface of adsorbate and adsorbent depending on solid acid-base composition of the surfaces of interacting components, closely connected as well to surface texture and water vapour content i.e. depending on specific solid acid-base interaction mode. Specifically, the surface of higher oxidation state species of adsorbate is attracted to alumina constituents of the respective zeolite starting dealumination and beginning to form (in presence of traces of water vapour) ionic aluminum- metal oxyanion surface interaction product.

At relatively high concentration of deposited adsorbate, and as a result of advanced dealumination referred to above, it is expected that the whole surface area (including the surface of internal channels) could be virtually completely covered with the adsorbate

The type of interaction between adsorbed molecule and the solid surface varies over a wide range from weak nonpolar van der Waals forces to strong chemical bonding "chemisorptions"[3, 4]. On one hand, chemisorptions is highly specific in nature and depends on the chemical properties of both surface molecules and adsorbed molecule and since chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer on the surface of substrates [3,4]. Adsorption arising from weaker van der Waals and dipole forces on the other hand is not specific in character and can take place in any system (that is in different crystalline or semi-crystalline species of deposited adsorbate). It is to be expected that surface interacting components will intensively chemisorb and strongly react chemically with increasing temperature with the result of apparent shifts of characteristic bands of interacting components to higher wave numbers

accompanied by broadening, lowering or virtual disappearance of their intensities along with different fine structure and additionally resulting in possible formation of reaction products reflected in emergence of new characteristic vibrational bands. It is also postulated here that this shift of vibrational absorption bands of interacting bonds to higher wave numbers, which have been repeatedly measured by different authors in the field of adsorbed gases e.g., for silanol bands, and also in case of liquid and solid phases, results in characteristic vibrational bands of possible reaction products which are due to local electron density at the periphery of surface interacting components increasing the force constants and hence the bond order of surface interacting vibrational modes.

In other words, the structure differences in size and shape of adsorbate crystallites and partial breakdown of intrazeoltic structure of adsorbent due to mutual solid-solid interaction as in case of starting dealumination is also manifested in shifts of characteristic bands of interacting components[5] to higher wave numbers accompanied by broadening, lowering or virtual disappearance of their intensities along with different fine structure. Possible formation of reaction products will be likewise reflected in emergence of new characteristic vibrational bands. As will be detailed in section V, the structural differences in size and shape of surface interacting components which are also responsible for these spectral changes are also responsible for Lewis and Brönsted acid sites – easily detected by vibrational spectroscopy[6]. In this context, coordinatively unsaturated sites are the cause of Lewis acids sites whereas higher dispersion, higher aggregation of multi-layers of adsorbate having higher oxidation state accompanied by water vapour content therefore is responsible for Brönsted acidity. Possible reaction products can also have both Lewis and Brönsted acid sites depending on their constitution and structure. Both kinds of acidities are the reason for specific type of catalytic action of loaded zeolites. All the above mentioned factors together with kind and nature of bonding which as outlined may range from weak van der Waal forces to specific chemisrption have to be considered when visualizing a surface model including chemisorbed and various physically adsorbed species.

Finally, higher oxidation species of interacting adsorbate can react with silica surface hydroxyls to probably produce uniform structures probably of first isolated monomers tetrahedrally coordinated oxyanion monomer species[5]. Chromium is known to exist as monomeric $[CrO_4]^{2-}$ within the supercages of zeolites with no substantial collapse of lattice in oxidized chromium-exchanged zeolites[7-9], therefore not easily forming isopolyacids and accordingly not in a situation to form

heteropolyacids. Thorough and uniform distribution of adsorbance monolayer is logically achieved only at low adsorbent loading, since higher loading creates crystal building forces of adsorbate drawing, pulling and attracting deposited molecules to grain, therefore bringing about bigger crystallites and thereby overwhelming monolayer solid-solid adsorption. However, in case of chemically stable but at the same time polarizable adsorbates like Mo, W or V oxyanions easily forming dimmers and depending on ambient acidity higher polymeric isopolyacids may be formed .These isopolyacids are liable for heteropolyacid formation by surrounding the central Si atom (Si center anion coordinated to Mo, W or V anions) most frequently in the ratios 1:12, 1:9 and/ or 1:6, where other coordinations are also possible[7]

Vibrational spectral manifestations of the above structural features

The vibrational spectra of molecules in crystals are not very different from the corresponding frequencies in the gaseous state[10-13], but other differences arises[1], for example the tetrahedral vibrational bands of zeolites $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ will be subjected to static filed and correlation field effects[1].

Si-O-Si bonds of zeolites posses intense adsorption in the ~ 1100-1000 cm^{-1} region[5]. Another broad (evidently because of hydrogen bonding) band appears with center at about 1000 cm^{-1} and which shifts appropriately on deuteration[6, 14, 15] and therefore may be described as surface Si-OH deformation.

Typical infrared vibrational bands of NaY zeolite are the absorptions at 1140, 1000 (very strong), 900-920 (shoulder), 800, 705,585,465 (strong), and at 380 cm^{-1}. The bands at 1000, 705 and 465 cm^{-1} are due to internal vibrations of $(Si,Al)O_4$ tetrahedra; the other bands at 1140, 800,585 and at 380 cm^{-1} are attributed to external[8,10] linkages (correlation field effect) between (Si, Al) O4 tetrahedra and hence are related to framework structure. All these bands of variable intensity and width depend on the temperature i.e. on calcination procedures[11]. As stated above both double rings forming hexagonal prisms as well as pore-openings are controlled by Si/Al ratio of the zeolites. Absorption in 650-500 cm^{-1} region is attributed to double rings, whereas absorption in the 420-300 cm^{-1} region is connected to large opening of zeolite windows. Observed bands at 810 and 457 cm^{-1} are assigned to siloxane linkage whereas absorptions at 601 and 488 are related to 4-fold siloxane rings[12-15]

For multivalent ion species adsorbate of e.g. central atoms V, Cr, Mo and W., outlined above, temperature elevation results in chemisorption which will be manifested under the above mentioned conditions, in beginning dehydration of interacting components and also in starting dehydroxlyation of the Si-OH of zeolites forming oxygen bridged bonds between Si and the reacting higher-valent metal species accompanied with appreciable dealumination and parallel loss of crystallinity and beginning breakdown of zeolite framework. Advanced delumination would thus lead to disappearance of zeolite surface absorption bands belonging to Si-OH at about 1000 cm^{-1} with its wings so that this absorption region is more or less clear and therefore relatively easy to analyze possible solid-solid interaction products absorptions in this region. Beside δ Si-OH at about 1000-970, the vibrational intensities of zeolite Si-OH bands at about 3600 cm^{-1}, and those of Al-O bands[6] at ~ 758 cm $^{-1}$, are expected to start to diminish or virtually disappear. As mentioned before, antisymmetric vibrations of zeolite framework at ~ 1010 cm^{-1} and asymmetric bands of reacting components should be more strongly affected than the corresponding symmetric vibrations. The change in intensity which may occur in zeolite asymmetric vibration at ~ 1010 cm^{-1}, should be accompanied by shift towards higher frequency with increasing surface coverage [8]. These effects are explained as follows: Differences in local electron density, especially at the periphery of the adsorbate molecules, cause significant change [6] in the nature of interaction with the zeolite and in the energies of interaction, even for adsorbate with closely related geometrical structure. It is excepted therefore to detect tetrahedra vibrations V-O at 804 cm^{-1}, Cr- O at 890 cm^{-1}, Mo-O at 897 cm^{-1} and W-O at 931 cm^{-1}; and M-O-Si bands which absorb for the metal species V, Cr, Mo and W also in the same crowded spectral region between 1000 and 900 cm^{-1}. Under favorable conditions, calcined metal oxides $M^{n+}_2O_n$ which understandably absorb higher in wave number are expected to be also detected in the neighboring region.

In case of vapour deposition using metal carbonyls $M(CO)_n$, which assures better metal dispersion and accordingly more extensive solid-solid interaction; decomposition of the respective carbonyl can take place at the channels, at the pore opening and/or at the outer surface of the individual zeolite. The ratio of decomposed/ undecomposed metal carbonyl could indeed be correlated with the geometrical structure and dimensions of both metal carbonyl and zeolite. The extent of decomposition can be identified through carbonyl subspecies [16] and Raman spectroscopy can help in identifying possible undecomposed rest of metal carbonyl through the emergence of respective symmetric bands of corresponding metal

carbonyl. In case of oxidation or decomposition of byproduct CO, it is foreseen that oxalate $C_2O_4^{--}$, formiate HCO^{-2} and hydrolysis products of CO_2 e.g. HCO_3^- and CO_3^{2-} species may result. Oxalate bands at 1640 and 1450 cm^{-1} can overlap both with the high frequency wing of water vapour deformation vibration centered at 1628 cm^{-1} and also can overlap extensively [17] with other zeolite bands. On the other hand, the presence of carbonate could be established through the emergence of as CO_3^{--} in the 1429 region [17]. In case of presence of CO_3^{2-}; bicarbonate must also be present which could be identified by δ as HCO_3^- at 698 cm^{-1}, a band which does not overlap significantly with zeolite i.r absorptions. The process of carbonmonoxide oxidation which normally takes place only at higher temperature, is catalyzed in the presence of zeolite loaded with highly dispersed multivalent metal species at relatively lower temperatures. This catalyzed carbon monoxide oxidation is apparently possible because in case the extent of carbonyl decomposition is complete, metals also in their dispersed and hence in their catalytically active state will result. On the other hand and according to reaction conditions, oxidation of decomposition products of metal carbonyls can also result. These oxidation-reduction reactions can be followed up visually through the colors of different oxidation states of the adsorbed respective multivalent metal species [1,8,19]: e.g. V^{5+} white and yellow, V^{4+} blue, V^{3+} peach blossom red, V^{2+} gray violet & Mo^{6+} - Mo^{5+} deep blue, Mo^{4+} green black, Mo^{3+} deep red, Mo^{2+} yellow & W^{6+} white, W^{6+} - W^{5+} blue, W^{3+} light brown.

Acid sites

From section III, it is to be anticipated that Lewis acidity, could be generated for zeolites under auspicious conditions and calcination procedures as a result of proper surface and texture changes whereas Brönsted acidity may be generated under favourable conditions of water vapour content. specifically, coordinativly unsaturated sites are the cause of Lewis acid sites whereas higher dispersion, higher aggregation of multilayers of adsorbate having higher oxidation state and water vapour content thereof is responsible for Brönsted acidity. The reason for manifestation of Brönsted acidity is on one hand higher condensation of oxianios to form isoploy-and/or heteropolyanions which goes parallel with ambient hydrogenion acidity and on the other hand water vapour content reacts with higher oxidation states of metal ions forming Brönsted acids. As a result of surface solid-solid interaction at higher temperatures and as a consequence of subsequent intrazeolitic dealumination, it is expected that, coordinativly unsaturated sites of Al will decrease with the possible generation of other Lewis sites through formation of new products and new phases as a result of surface reactions. Beside the above mentioned reaction

conditions and structural characteristics of surface reacting components and product phases, it is expected that the Brönsted to Lewis acid sites ratio (B/L ratio) is also a function of oxidation state of adsorbate metal species being namely lowered in case of chemical reduction of that species[20,21]. Evaluation of amount, strength and nature (Brönsted or Lewis sites)[22] is important for specific type of catalytic action of loaded zeolites. Lewis bases, for example pyridine molecules adsorbed on Lewis-acid sites form complexes (PyL) for which the 1457 cm^{-1} i.r bands is characteristic; the reaction with Brönsted-acid sites lead to the formation of pyridinium ions (PYH$^+$) characterized by the band at 1545 cm^{-1} [2,21,22].

Other Physiochemical methods

To further help identify the different dispersion and hence interaction mode of encapsulated multivalent metal species, other physiochemical methods should be utilized beside vibrational spectroscopy. X-ray powder diffraction patterns (XRD) are expected to show decrease in reflex intensities belonging to specific zeolite with increasing loading and upon increasing dispersion as a result of decreasing crystallinity. Difference in reflex intensities and sharpness means differences in detailed angles and bonding[23]. Surface area measurements and water content (obtained from weight loss upon calcination) are expected to go homogeneously parallel to XRD in so far as they decrease with increasing adsorbent coverage [8] which would indicate beginning breakdown of the respective zeolite.Transmission Electron microscopy can show the crystallization state of both substrate and coverage aggregates.

In order to further examine adsorbate dispersion and its possible location; extraction procedures can be utilized. In extraction procedures with suitable solvents; outersurface /cavity ratio adsorbed species[8] as well as state of distribution of adsorbate as a function of coverage concentration can be evaluated.

Ultraviolet diffuse reflectance spectra can distinguish between species in tetrahedral (monomeric) and octahedral (polymeric) coordination [8]. Reflectance spectroscopy and temperature programmed reduction can also be utilized; temperature programmed reduction and H_2 uptake procedures[11] are capable of identifying tetrahedral coordination symmetry and tetrahedral/octahedral proportion in as much as tetrahedral structure is less easily reducible than octahedral symmetry therefore a method of identifying intrazeoletic dispersion.

Finally, the distribution of adsorbate dispered aggregates between cages, hexagonal prisms and outer surface as a function of temperature and pressure gradient-between surface and internal channels-can be studied in conjunction with the above mentioned physiochemical methods either by utilizing electron spin resonance which gives information about valency and bonding of possible existing unpaired electronic state [11] or by taking advantage of X-ray photoelectron spectroscopy which is capable of revealing the electronic energy levels of component atoms and hence their boding characteristics. Recently, [24] dielectric experiments as well as DTA measurements have been used to give evidence of adsorbate distribution inside pores/cavities in zeolites.

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