Acid sites topology in aluminas and zeolites from high-resolution solid-state NMR

A.L. Blumenfeld and J.J. Fripiat

Department of Chemistry and Laboratory for Surface Studies, The University of Wisconsin-Milwaukee, Milwaukee, WI 53201, USA

High-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy is recognized as one of the most powerful tools in characterization of acid catalysts. Hundreds of research papers and tens of reviews and monographs appear each year. It is evidently an impossible task not only to discuss all recent contributions but even to mention each of them. Therefore, we restricted ourselves to a rather narrow (but fast developing) field, namely, the characterization of surface topology of real catalysts by heteronuclear dipolar interaction between magnetic nuclei. The common desire of all spectroscopists to obtain spectra with the best possible resolution competes with the general trend to obtain the greatest amount of information on systems. In this review we outline experimental approaches to this problem and describe several editing techniques which introduce new dimension into conventional NMR. The discussion is furnished with examples from current literature, however the emphasis is given to our recent publications in which the introduction of new experimental approaches resulted in deeper insight into the nature of surface acidity. In particular, two problems are discussed in detail, namely, how to observe selectively surface species (cross-polarization experiments) and how to retrieve dipolar contribution from the overall line shape (double-resonance spin-echo experiments). The results obtained from these experiments allowed us to reach important conclusions concerning the nature of Lewis acidity in aluminas and the role of isolated Al atoms in formation of Bronsted sites in zeolites.

Keywords: topology; acid sites; NMR

1. Introduction

Knowledge of the physical features of a region of the surface and the properties of the atomic configurations is the ultimate goal of a topology study. The aim of this contribution is to show that different techniques belonging to the domain of nuclear magnetic resonance are among the most successful tools for characterizing the topology of acid sites in aluminas and zeolites.

The term “topology” used in this review deserves clarification. Evidently, it has nothing to do with a fascinating branch of modern mathematics which tries to reveal the most fundamental properties of the space, but rather disguises our inability to give an unambiguous structural description of the disordered surface of a real catalyst. The disorder results from the thermal activation which transforms an almost inert solid (the “perfect” zeolite) into a catalyst. Depending on the nature of the acid centers, either Bronsted or Lewis, the experimental strategy to describe them may change appreciably.

The first obvious approach to the study of Bronsted acidity is to observe the $^1$H magic angle spinning (MAS) spectra and to identify the acidic hydroxyls through the chemical shifts of $^1$H lines [1–3]. Downfield shifts smaller than 2.5 ppm are due to nonacidic or weakly acidic OH groups. The acidic OH groups have shifts larger than 4 ppm. Although this information has contributed to the knowledge of zeolites, it does not provide a topologic description. The acidic OH bridges aluminum to silicon in the tetrahedral network and the Al–H distances have been obtained within 0.05 Å from the analysis of the $^1$H spinning sidebands [4]. This technique applied to various zeolites has shown that the Al–H distance is a function of the number of oxygen atoms of the oxygen rings [3]. Such information may be considered as topological, but so far basic questions such as the relationship between the acid strength and the atomic surrounding of the bridging oxygen or, for instance, the number of aluminum in the silicon first coordination shell are not answered.

In zeolites this first coordination shell may contain up to four aluminum. Thus, in the corresponding H-zeolite there is an OH accumulation in the (Si–nAl), $n > 1$, clusters of atoms. The consequence, therefore, is to render the structure more fragile and to favor the clustering of nonframework aluminum (NFAI) upon thermal activation. It has, indeed, been observed experimentally that the intensity of the $^4$O(Si–nAl) ($n > 1$) contributions to the $^{29}$Si spectrum decreases more rapidly as the amount of NFAI increases, than that of the $^4$O(Si–1Al) contribution [1,5].

Another expected consequence of a local OH accumulation is the lowering of the acid strength. It has been widely documented that a decrease of the overall amount of framework aluminum (FAI) results in an increase of the acid strength of the remaining OH [6].

A general topological information at the scale of the Si first coordination shell is, thus, available from the deconvolution of the $^{29}$Si MAS spectrum, since it gives the number of silicon atoms having up to four aluminum atoms in the first coordination shell.
It would be very interesting to explore this shell in choosing a bridging proton as observatory. Experiments with this as a goal have been achieved by Haw and collaborators [7] who observed the \(^1\)H line with \(^{27}\)Al partial decoupling (quadrupolar ticking). This kind of experiment allowed them to show unambiguously that the acidic protons in HZSM-5 (NMR Si/Al ratio \(\approx 19\)) with resonances at 4.3 ppm and at 5.9 ppm are linked to aluminum. The 1.6 ppm difference in chemical shifts suggests that the environments of the two kinds of protons have quite a different electronegativity. On the same HZSM-5, Kenato et al. [8] used SEDOR (spin-echo double resonance) technique in order to obtain Al-H distance and got practically the same value as that obtained through analysis of the \(^1\)H sidebands reported above.

Another approach for answering questions about the molecular environment of an acid site is to observe the interaction between a molecular probe and its environment. This may include a transformation of the molecular probe such as protonation. The advantage of this approach is to provide a way of quantifying the number of sites or the acid strength. Protonation of pyridine and ammonia can be followed quantitatively by infrared spectroscopy [9], as well as by \(^1\)H NMR [1].

This approach cannot be used to identify the molecular grouping which constitutes “a site”. However, if either \(^{13}\)N or \(^1\)H of chemisorbed NH\(_3\) can be magnetically polarized, then two techniques can be used to observe the neighboring \(^{27}\)Al. The most obvious method is through the use of simple cross-polarization (CP) which has been applied in order to observe Lewis sites in aluminas and dealuminated acid zeolites [10,11]. The \(^1\)H polarization of chemisorbed ammonia is transferred to nearby \(^{27}\)Al giving information on the coordination states.

The technique used for the topology study of Bronsted sites is another version of double resonance application [5]. This technique is the rotational echo double resonance (REDOR) in which the excitation of \(^{29}\)Si was operated by CP in order to get rid of all silicon which are not influenced by chemisorbed ammonia or NH\(_3\). It gives access to the heteronuclear dipolar interaction or heteronuclear second moments and, in turn, it permits elaboration of models of NH\(_3\) chemisorption on Bronsted acid sites in the Si-\(\alpha\)Al clusters.

Since NH\(_3\) is the molecular probe used so far in our topological studies, it is worthwhile to recall briefly what is known about its behavior towards Lewis and/or Bronsted acid sites. The majority of the information comes from infrared spectroscopic investigations which date back to the end of the fifties [9].

Gaseous NH\(_3\) has four fundamental modes of vibration (point group \(C_6v\)), all Raman and infrared active [12]. The totally symmetric bending \(v_2\) split by inversion doubling is at \(\sim 950\) cm\(^{-1}\) and is very sensitive to the environment. Its frequency increases linearly with the square of electronegativity of the Lewis site [13,14]. Unfortunately, this mode cannot be observed by IR in all zeolites, because it overlaps with SiO vibrations of the zeolite lattice. Fortunately, the asymmetric stretch \(v_3\) at 1620 cm\(^{-1}\) is always observable but if it is used quantitatively in order to count the number of Lewis sites, one has to ensure that all physisorbed ammonia is gone. In a study to be published later [15], it will be shown that the Lewis site NH\(_3\) adduct \(v_2\) has been observed in alumina (at 1250 cm\(^{-1}\)) and in several zeolites above or around \(\sim 1300\) cm\(^{-1}\).

Two IR active vibrational modes \(v_4\) and \(v_3\) of NH\(_4^+\) are characteristic of the generally accepted T\(_d\) symmetry [1]; both are triply degenerate. The “useful” mode is \(v_4\) near 1450 cm\(^{-1}\) because it is located in a transparent window of the IR domain in zeolites or aluminas and its extinction coefficient, as well as that of the \(v_4\) bending of chemisorbed ammonia, are known [16]. Then, the quantization of the number of sites is possible.

A lowering of the NH\(_4^+\) symmetry from T\(_d\) to C\(_{3v}\) has been suggested in clays [17,18]. Such a change in symmetry would lift the degeneracy of \(v_4\). On some zeolites (USY, for instance), an intense shoulder is observable at 1430 cm\(^{-1}\) [19]. Since a high frequency CO stretching mode has also been observed for these samples between 2173 and 2177 cm\(^{-1}\) and attributed to strong Bronsted sites [20], the shoulder at 1430 cm\(^{-1}\) may represent NH\(_4^+\) formed on these sites, for which the proton transfer is total.

The NMR techniques used here, MAS CP \(^1\)H(NH\(_3\))\(^{27}\)Al or MAS CP REDOR \(^1\)H(NH\(_3\))\(^{29}\)Si, have in common the requirement that the probe molecule should not translate on the surface at the time scale of the experiment in order to have an efficient polarization transfer.

In a NH\(_3\):L adduct, with chemisorption energy larger than \(\sim 150\) kJ/mol [21,22], translation is improbable, however rotation around the C\(_{3v}\) axis should not be severely restricted.

The situation for Bronsted sites is different, at least in the case of a total proton transfer. The surface diffusion might be not negligible at the time scale of the NMR measurements, but it has been shown that for NH\(_3\)Y it is negligible as long as the zeolite is thoroughly dehydrated [23,34]. This condition should be fulfilled for REDOR studies.

The two classes of materials reviewed here are characteristic of amorphous (alumina) or crystalline (zeolites) materials. The rationale for this choice is the following. When an acidic zeolite is calcined, a fraction of the framework aluminum (FAI) is transformed into nonframework aluminum (NFAI). NFAI exists as nanosized particles which are within the porous system of the zeolite [25]. These particles have aluminum in tetrahedral (IV), pentahedral (V) and octahedral (VI) coordinations with respect to oxygen [26,27]. As observed in transition alumina, NFAI is most probably the seat of Lewis sites.