

Assignment

Course : Principles of Surface Analysis

NMR Spectroscopy

Submitted by

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NMR Spectroscopy

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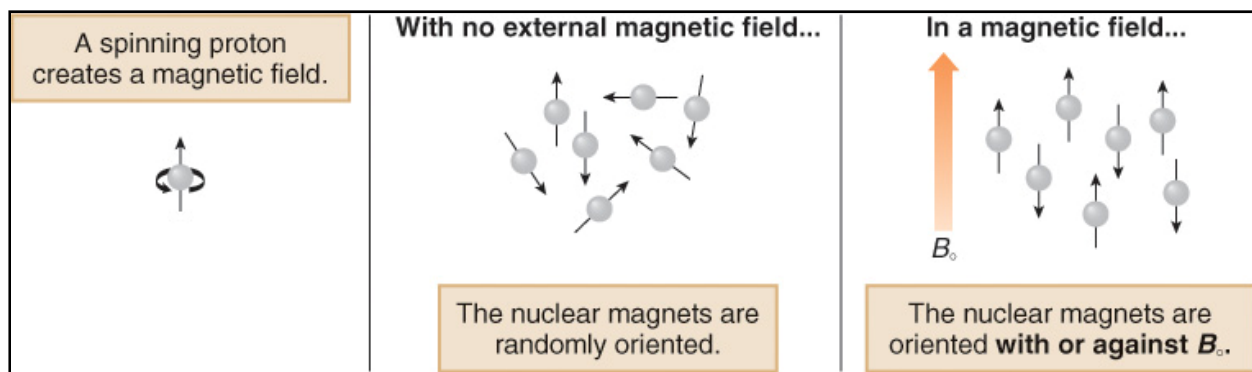
NMR Spectroscopy

1. NMR Theory:

NMR spectroscopy is applicable to any nucleus that possesses a magnetic moment, i.e. a nuclear spin.

- When a charged particle (such as a proton) spins on its axis, it creates a magnetic field. Thus, **the nucleus can be considered to be a tiny bar magnet**.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0 , they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.
- The energy difference between these two states is very small (<0.1 cal).
- Spin quantum number, I : 0, 1/2, 1, 3/2, 2,

$I=0$	$^{12}\text{C}, ^{16}\text{O}$
$I=1/2$	$^1\text{H}, ^{13}\text{C}, ^{15}\text{N}, ^{19}\text{F}, ^{31}\text{P}$
$I=1$	$^2\text{H}, ^{14}\text{N}$



^1H , ^{13}C , ^{15}N and ^{31}P nuclei are suitable isotopes allowing the study of a wide variety of reactants and adsorbate complexes interesting for studies in the field of heterogeneous catalysis.

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Due to their nuclear spin of $I = 1/2$, sufficient line narrowing is reached by the conventional high-resolution solid-state NMR techniques. Similar conditions exist for ^{29}Si and ^{31}P nuclei occurring in the framework of solid catalysts.

Isotopes with a nuclear spin $I > 1/2$, such as ^7Li ($I = 3/2$), ^{11}B ($I = 3/2$), ^{17}O ($I = 5/2$), ^{23}Na ($I = 3/2$), ^{27}Al ($I = 5/2$), ^{71}Ga ($I = 3/2$) and ^{133}Cs ($I = 7/2$), are additionally characterized by an electric quadrupolar moment. These nuclei are involved in quadrupolar interactions, making their investigation more complicated.

In all of the above cases, solid-state NMR spectroscopy is a very useful tool for

- the investigation of framework atoms
- extraframework species
- surface sites of solid catalysts and of adsorbate complexes
- reaction intermediates formed on these materials.

In a magnetic field, there are now two energy states for a proton:

1. **lower energy state** with the nucleus aligned in the same direction as B_0
2. **higher energy state** in which the nucleus aligned against B_0 .

When an external energy source ($h\nu$) that matches the energy difference (ΔE) between these two states is applied, energy is absorbed, causing the nucleus to “spin flip” from one orientation to another.

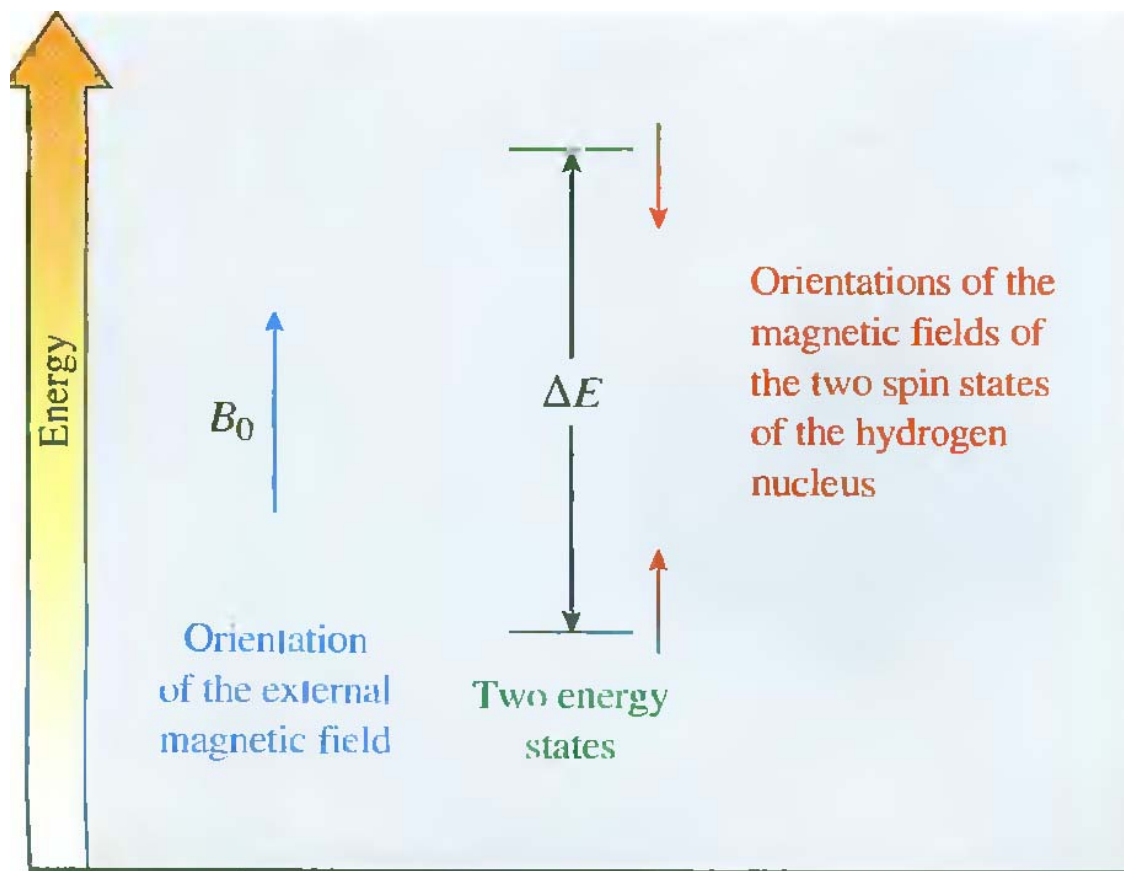
The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.

Thus, two variables characterize NMR:

Applied magnetic field B_0 : measured in tesla (T)

Frequency ν : Radiation used for resonance, measured in hertz (Hz), or megahertz (MHz) - ($1 \text{ MHz} = 10^6 \text{ Hz}$).

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Nuclei characterized by a spin I possess a nuclear magnetic moment $\mu = \gamma \cdot hI$, where γ is the magnetogyric ratio and h is Planck's constant h divided by 2π . When placed in an external magnetic field B_0 , the Zeeman interaction quantizes the orientations of the nuclear magnetic moments accompanied by a splitting of the energy level system into $2I + 1$ eigenstates with energies

$$E(m) = -m \cdot \gamma \cdot \frac{h}{2\pi} B_0$$

where $m = (I, I - 1, \dots, -I)$ is the magnetic quantum number.

Transitions between neighboring energy levels can be induced by an electromagnetic radiation, if the radiation frequency ν agrees with the Larmor frequency.

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

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Nowadays, NMR spectroscopy is performed in external magnetic fields with flux densities of up to $B_0 = 21.1$ T, corresponding to the Larmor frequencies of ^1H nuclei of up to $\nu_0 = 900$ MHz.

Nuclear spin ensembles in liquids and gases cause narrow NMR signals since the influence of spatially anisotropic spin interactions on the linewidth is averaged to zero by isotropic motions.

In contrast, solid materials such as catalysts and adsorbate complexes give NMR spectra that are strongly affected by the anisotropic spin interactions.

The analysis of solid-state NMR signals occurring at characteristic resonance positions and having characteristic lineshapes is a source of structural information.

On the other hand, to reach a separation of the NMR signals of nuclei in different local structures and different chemical surroundings, sophisticated experimental techniques allowing an averaging of the nuclear spin interactions must be applied.

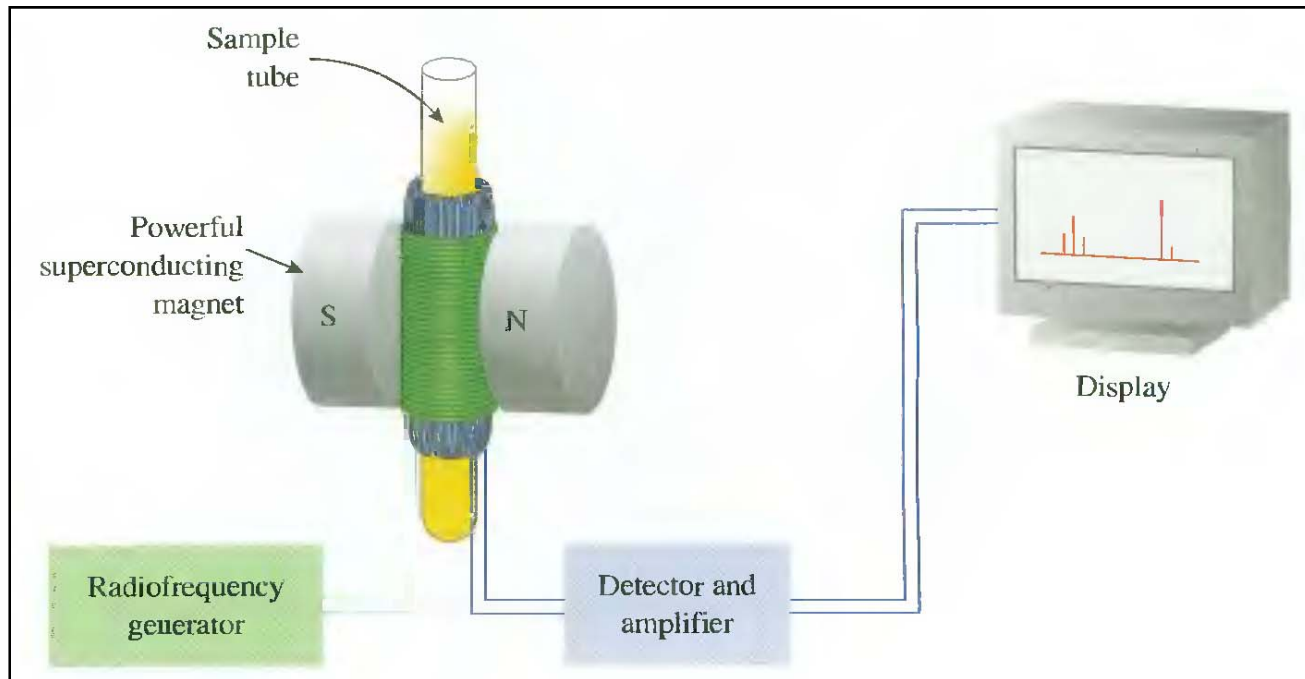
- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength B_0 , and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as ^1H , ^{13}C , ^{19}F and ^{31}P) or odd atomic numbers (such as ^2H and ^{14}N) give rise to NMR signals.

2. NMR Spectrometer Assembly :

- The sample is dissolved in a suitable solvent and placed in a thin glass tube. The tube is placed between the poles of the powerful supermagnet.
- In original instrument Frequency of the electromagnetic radiation in the radio region is held constant and strength of the magnetic field is also varied.
- When the magnetic field strength matches with the difference between the energy states then the proton is said to be absorbing the energy and is said to be in resonance.
- In modern instrument the magnetic field is held constant and the sample is irradiated with a brief pulse of radio-frequency irradiation.
- All nuclei are excited simultaneously. As the nuclei return to their equilibrium population a complex signal is generated.

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- A computer converts this complex signal to the normal spectrum using a mathematical treatment called a Fourier Transformation (FT). The advantage of FT-NMR is that the signal can be obtained in few seconds and this allows the signal averaging to be used to increase the quality of the spectrum.



3. Experimental Techniques of Solid State NMR Spectroscopy :

1. **Magic Angle Spinning (MAS):** involves fast sample rotation around an axis in the “magic” angle of $\theta_m = 54.7^\circ$ to the direction of the external magnetic field B_0 . having a gas bearing system for the rotor. Often, the rotors are made from zirconium dioxide. Depending on the rotor diameter, which is commonly between 7 and 2 mm, spinning frequencies between 5 and 35 kHz, respectively, can be achieved. Second order quadrupolar broadening is present.
2. **Double Oriented Rotation (DOR):** Involves simultaneous sample spinning around two axis. The experimental device consists of a large outer rotor reaching a spinning frequency of upto 1.5 kHz and small inner rotor with the spinning frequency of 7 kHz. The angle θ_1 between the external magnetic field and the rotational axis of the outer rotor corresponds to the magic angle θ_m . The angle θ_2 between the rotational axes of the inner and the outer rotor amounts to 30.5° . The advantage is total suppression of second order quadrupolar coupling.
3. **Multiple-Quantum MAS (MQMAS) Technique :** enhances the resolution of spectra due to nuclei with a half-integer spin $I > \frac{1}{2}$.
4. **Cross – Polarization (CP) experiment :** Increases the sensitivity significantly.

- 5. SEDOR, REDOR, TRAPDOR and REAPDOR Experiments:** SEDOR (spin echo double resonance), REDOR (rotational echo double resonance), TRAPDOR (Transfer of population in double resonance), REAPDOR (Rotational echo adiabatic passage double resonance.)

4. Preparation of the sample for NMR Spectroscopy:

Most solid-state NMR investigations of the framework of solid catalysts performed in the past decades were made using hydrated materials. In this case, the powder sample is filled into the MAS NMR rotor without special treatment. Nowadays, commercial glass inserts are offered for all commercial MAS NMR rotor types. Into a 4- and 7-mm glass insert, ca. 25 and 100 mg, respectively, of catalyst powder can be filled. After calcination of the catalyst material under vacuum and loading with probe molecules or reactants, the glass insert is sealed at the waist and the obtained glass ampoule is inserted into the rotor.

Another frequently applied technique is based on the preparation of the solid catalyst directly inside the sample volume of a MAS NMR rotor. After filling the catalyst material into the MAS NMR rotor, the rotor is put into a fitting at the bottom of a special vacuum equipment. Upon calcination of the catalyst under vacuum and loading with probe molecules or reactants, the MAS NMR rotor is sealed with a gas-tight rotor cap inside the vacuum equipment. After the treatment of the catalyst, the powder material is filled into an MAS NMR rotor at the bottom of the equipment, sealed with a rotor cap from a plug rack and transferred to the NMR spectrometer.

The study of the mechanisms of heterogeneously catalyzed reactions by solid-state NMR spectroscopy requires a suitable technique for carrying out experiments under well-defined conditions. For investigations under flow conditions, two different techniques were introduced:

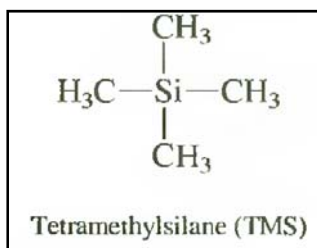
1. The catalytic reaction is performed in an external fixed-bed reactor, and subsequently the catalyst is transferred into an MAS NMR rotor after quenching the reaction.
2. In a true in situ technique, the MAS NMR rotor is used directly as a fixed-bed reactor situated inside a high-temperature MAS NMR probe.

5. Chemical Shift :

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in ppm (parts per million). Most protons absorb between 0-10 ppm.
- Chemical shift of the hydrogen signal that is the field required for hydrogen to be in resonance varies slightly with the chemical environment of hydrogen.

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- The terms “upfield” and “downfield” describe the relative location of peaks.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions. This peak occurs in the region of the spectrum where it does not usually overlap with the other absorptions.



In the plot of the acetone shown below the field strength increases from left to right. The protons of the TMS absorb at higher field than the most other protons thus TMS signal occurs at the right edge of the spectrum.

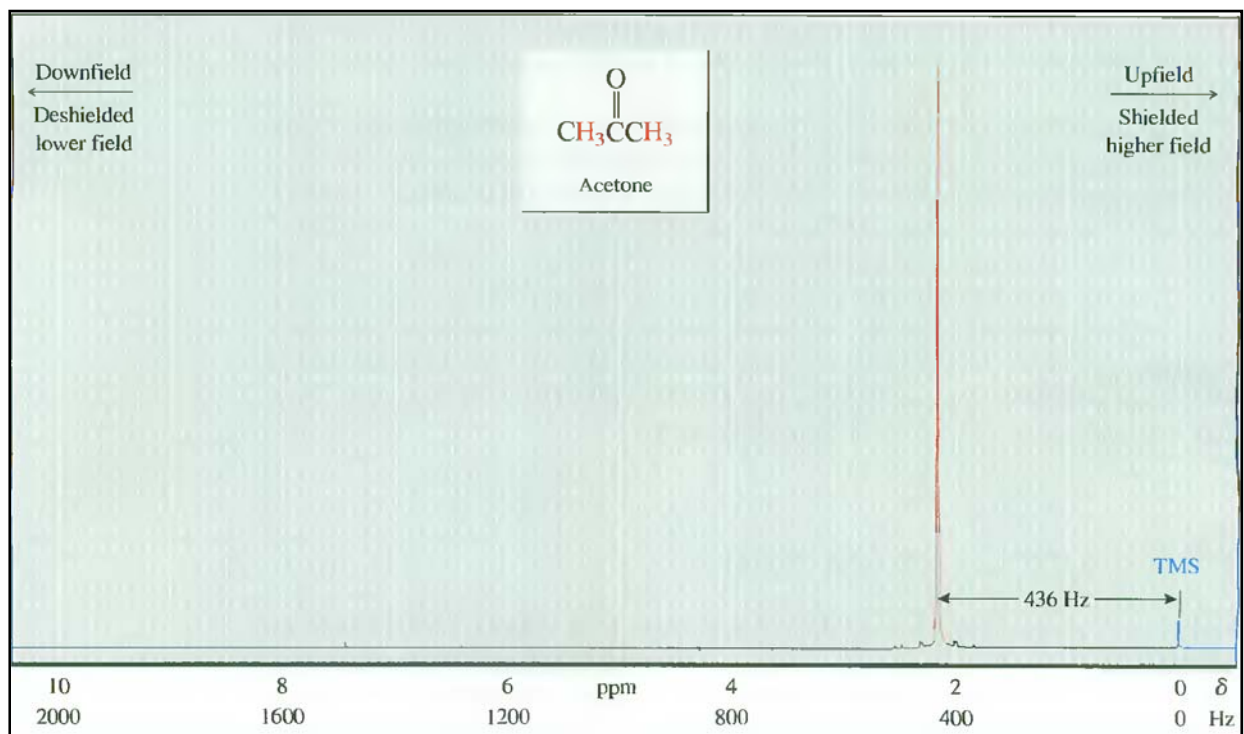
Energy separation of the two nuclear spin states is directly proportional to the magnetic field strength B_0 . That means the chemical shift is also directly proportional to the magnetic field strength. On the instrument with 4.67 T magnet which operates at the frequency of 200 MHz the peak for acetone occurs 436 Hz downfield from TMS. On the instrument with magnet twice as strong which operates at the frequency of 400 MHz the peak for acetone occurs at 872 Hz downfield from TMS farther downfield by factor of 2.

The chemical shift of the x axis gives the position of an NMR signal, measured in ppm, according to the following equation:

$$\delta = \frac{\text{Observed position of peak (Hz)}}{\text{Operating frequency of instrument (Hz)}} \times 10^6$$

By reporting the NMR absorption as a fraction of the NMR operating frequency, we get units, ppm, that are independent of the spectrometer.

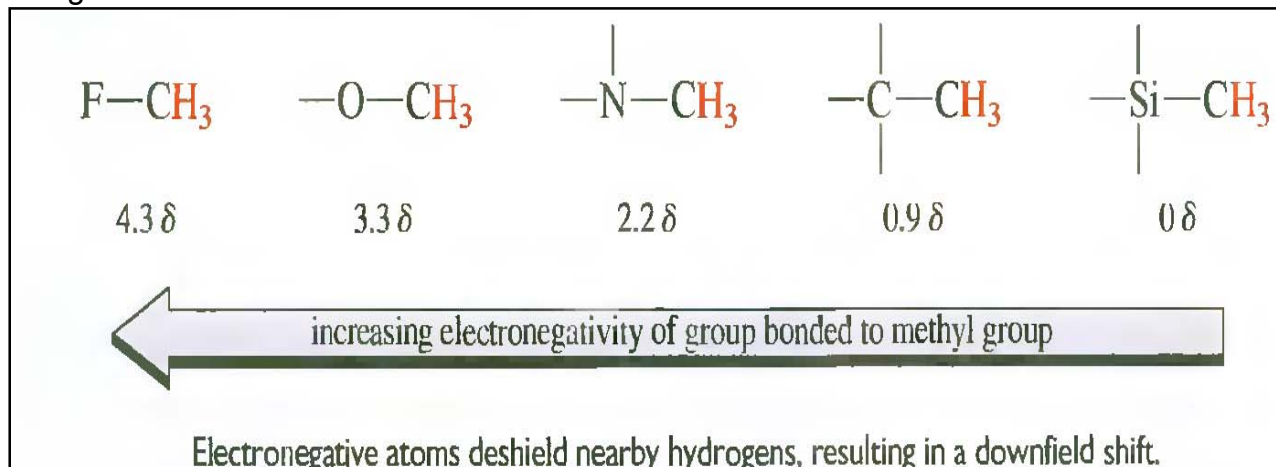
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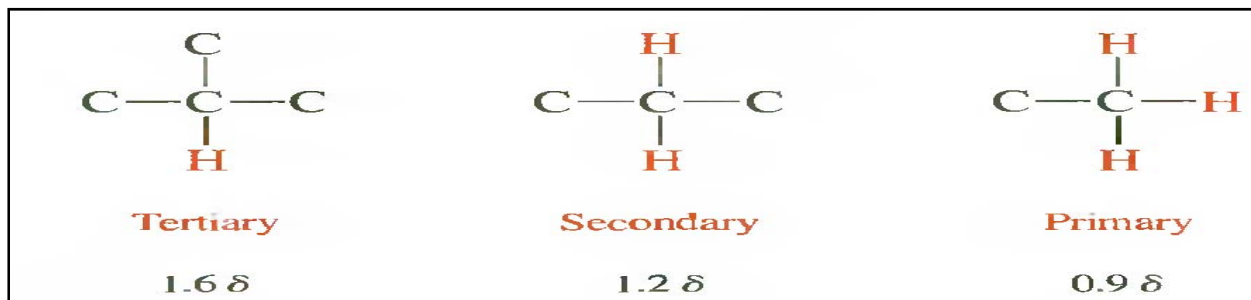
6. Trends in the chemical shifts

Inductive Effects

Consider the hydrogen bonded to the carbon. Its chemical shift depends upon the element which is attached to the carbon. If the element is electronegative then it pulls the electron density towards itself and deshields the hydrogen resulting in the absorption at higher δ .



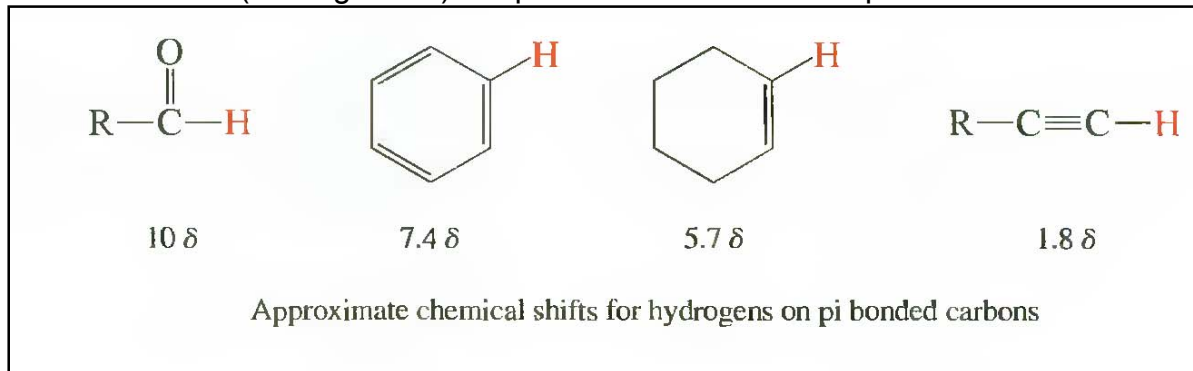
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The absorption of hydrogen attached to the secondary and tertiary carbon atom occurs more downfield.

Pi electron effects:

Electrons in pi MO's circulate more readily in the external magnetic field than those in the sigma orbital because they are less strongly held to nuclei. Depending on the exact geometry of the molecule the magnetic field of these circulating electrons will cause either downfield (on alignment) or upfield shift. This effect is pronounced in benzene.



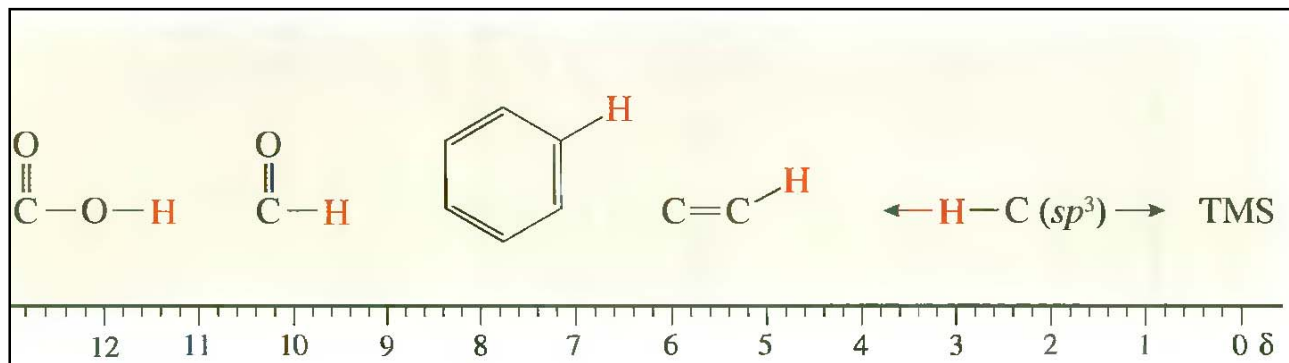
Larger shift in Benzene is due to "ring current effect". In case of aldehyde larger shift is observed due to higher inductive effect of oxygen while in case of acetylene upfield shift is observed because of circulating field of electrons opposes external magnetic field.

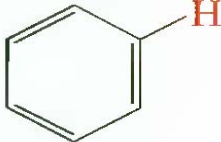
Hydrogen bonded to the heteroatom:

The chemical shift of hydrogens attached to oxygen and nitrogen depends upon the concentration and temperature because the extent of hydrogen bonding varies with these factors.

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Summary of chemical shifts:



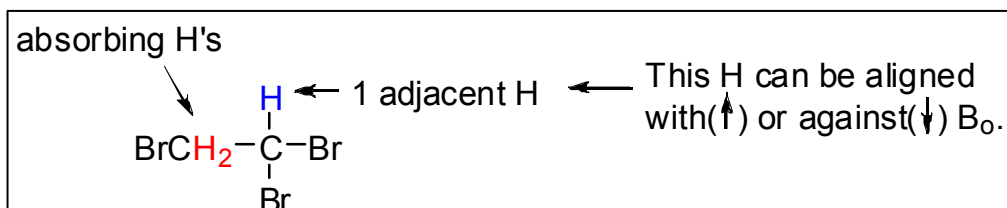
Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
—C—CH_3	0.9	Cl—CH_3	3.0
C=C—CH_3	1.6	O—CH_3	3.3
$\text{C}\equiv\text{C—H}$	1.8	$\text{O}=\text{C—O—CH}_3$	3.7
N—H	1–3	$\text{O}_2\text{N—CH}_3$	4.1
O—H	2–5	F—CH_3	4.2
R—O—C(=O)—CH_3	2.0	C=C—H	5.5–6.5
$\text{O}=\text{C—CH}_3$	2.2		7–8
N—CH_3	2.2	$\text{O}=\text{C—H}$	10
I—CH_3	2.2	$\text{O}=\text{C—O—H}$	12
$\text{N}\equiv\text{C—CH}_3$	2.2		
Ph—CH_3	2.3		
Br—CH_3	2.7		

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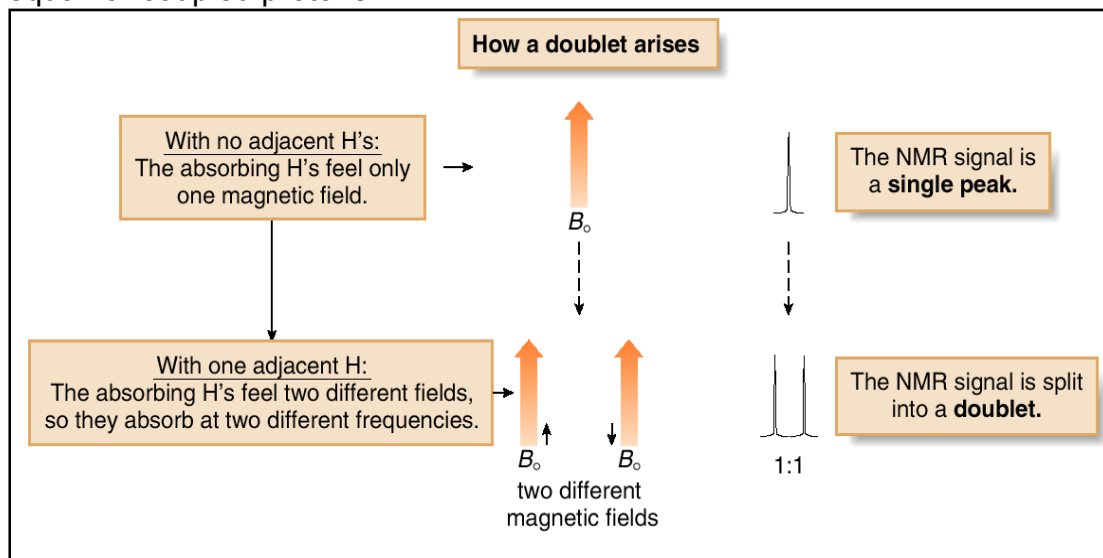
7. Spin coupling:

Each hydrogen can be considered as a small bar magnet. A particular hydrogen experiences the small magnetic fields of other nearby hydrogens in addition to the large magnetic field of external magnet. This results in the splitting of the absorption into multiple peaks. Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.

1. Doublet formation:



- When placed in an applied electric field, (B_0), the adjacent proton (CHBr_2) can be aligned with (\uparrow) or against (\downarrow) B_0 .
- Thus, the absorbing CH_2 protons feel two slightly different magnetic fields - one slightly larger than B_0 , and one slightly smaller than B_0 .
- Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.
- The frequency difference, measured in Hz between two peaks of the doublet is called the coupling constant, J . (usually in the range of 0 -18 Hz, independent of B_0)
- When two protons split each other, they are said to be *coupled*.
- The spacing between peaks in a split NMR signal, measured by the J value, is equal for coupled protons.

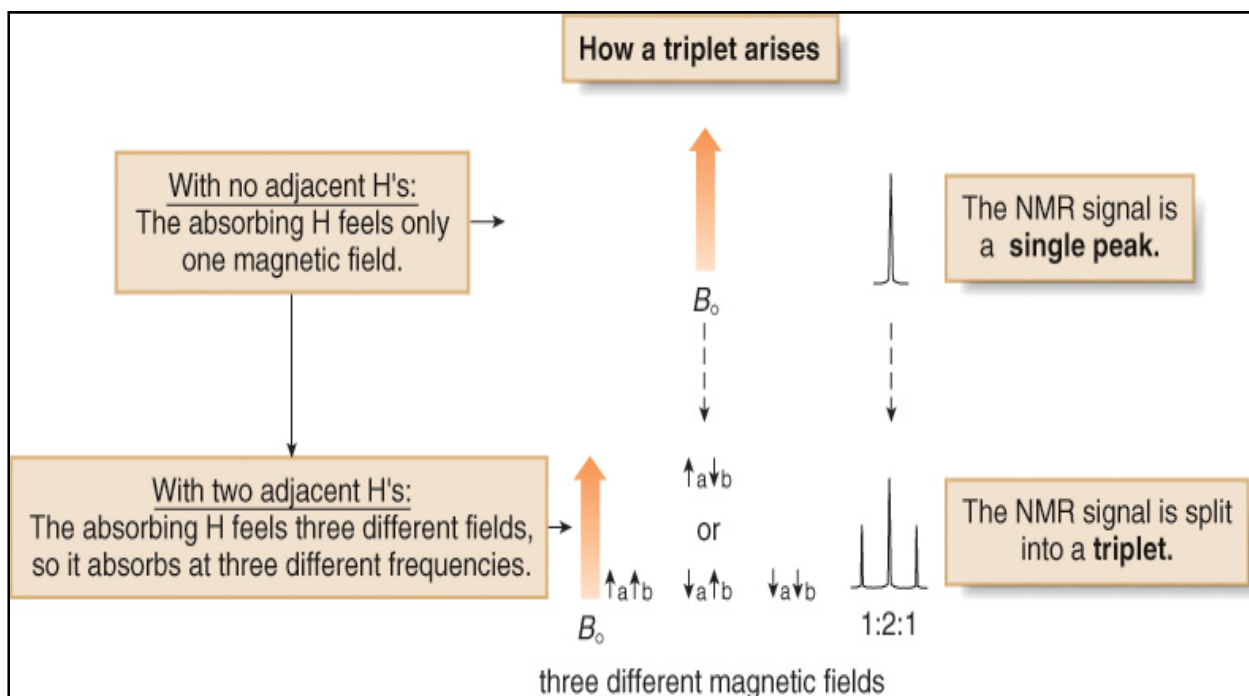


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2. Triplet Formation



- When placed in an applied magnetic field (B_0), the adjacent protons H_a and H_b can each be aligned with (\uparrow) or against (\downarrow) B_0 .
- Thus, the absorbing proton feels three slightly different magnetic fields - one slightly larger than B_0 , one slightly smaller than B_0 , and one the same strength as B_0 .
- Because the absorbing proton feels three different magnetic fields, it absorbs at three different frequencies in the NMR spectrum, thus splitting a single absorption into a triplet.
- Because there are two different ways to align one proton with B_0 , and one proton against B_0 —that is, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$ —the middle peak of the triplet is twice as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:2:1.
- Two adjacent protons split an NMR signal into a triplet.



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3. General rules:

Three general rules describe the splitting patterns commonly seen in the ^1H NMR spectra of organic compounds.

- Equivalent protons do not split each other's signals.
- A set of n nonequivalent protons splits the signal of a nearby proton into $n + 1$ peaks.
- Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

Splitting is not generally observed between protons separated by more than three σ bonds.

The quadrupolar interaction is observed only for nuclei with a nuclear spin quantum number $I > 1/2$ (e.g. ^{11}B , ^{17}O , ^{23}Na , ^{27}Al).

4. Complex Splitting:

Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the $n + 1$ rule to determine the splitting pattern.

Some facts about ^1H NMR spectra

- ***Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.***
- ***Even though each cyclohexane carbon has two different types of hydrogens—one axial and one equatorial—the two chair forms of cyclohexane rapidly interconvert them, and an NMR spectrum shows a single signal for the average environment that it “sees”.***
- **Benzene has six equivalent deshielded protons and exhibits a single peak in its ^1H NMR spectrum at 7.27 ppm.**

NMR Spectroscopy

Which Nuclei are Candidates?

In principle, each of the three basic atomic constituents of the aluminosilicate framework of zeolites - silicon, aluminium and oxygen - are amenable to MR measurements by its naturally occurring isotopes ^{29}Si , ^{27}Al , ^{17}O respectively.

Several other elements replacing silicon or aluminium in tetrahedral sites of the aluminosilicate framework of zeolites, such as phosphorous, boron, gallium, germanium, beryllium, vanadium, and others, can also be profitably studied by solid-state MR of their respective MR-active nuclides, for example ^{31}P , ^{11}B , ^{69}Ga , ^{73}Ge , ^9Be , ^{51}V .

Following is the table indicating the spin, natural abundance of the isotopes of the elements.

Isotope	Spin	NMR frequency (MHz) ^a	Natural abundance (%)	Relative receptivity ^b
^1H	1/2	400.00	99.985	1.000
^7Li	3/2	155.45	92.58	0.272
^{11}B	3/2	128.34	80.42	0.133
^{13}C	1/2	100.58	1.108	$1.76 \cdot 10^{-4}$
^{17}O	5/2	54.23	0.037	$1.08 \cdot 10^{-5}$
^{23}Na	3/2	105.80	100.00	$9.27 \cdot 10^{-2}$
^{27}Al	5/2	104.23	100.00	0.207
^{29}Si	1/2	79.46	4.70	$3.69 \cdot 10^{-4}$
^{31}P	1/2	161.92	100.00	$6.63 \cdot 10^{-2}$
^{51}V	7/2	105.15	99.76	0.38
^{133}Cs	7/2	52.46	100.00	$4.82 \cdot 10^{-2}$
^{205}Tl	1/2	230.83	70.50	0.140

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8. Parameters in NMR spectra:

Four different features of a ^1H NMR spectrum provide information about a compound's structure:

- Provided that well resolved signals appear in the NMR spectrum, the **number of signals** in the spectrum gives immediately the number of different structural environments of the observed nucleus present in the sample
- **Isotropic chemical shift** provides valuable information on the chemical environment of the resonance atom, such as number and type of neighboring atoms, coordination number, and bonding geometry.
- The **relative (integrated) signal intensities** correspond to the relative occupancies of the different environments. It must be noted, however, that for quadrupolar nuclei the line intensities obtained experimentally from MAS NMR spectra are not a priori proportional to the site populations but must often be corrected for possible contributions from satellite transitions and/or spinning side bands
- Quadrupole coupling constants, QCC, and asymmetry parameters of the EFG, η_Q cannot directly be obtained from the NMR spectra but have to be calculated.

The area under an NMR signal is proportional to the number of absorbing protons.

^{13}C NMR Spectroscopy:

^{13}C Spectra are easier to analyze than ^1H spectra because the signals are not split. Each type of carbon atom appears as a single peak.

The two features of a ^{13}C NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.

The number of signals in a ^{13}C spectrum gives the number of different types of carbon atoms in a molecule. Because ^{13}C NMR signals are not split, the number of signals equals the number of lines in the ^{13}C spectrum. In contrast to the ^1H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so ^{13}C NMR signals are not integrated.

^{13}C NMR absorptions occur over a much broader range (0-220 ppm).

The chemical shifts of carbon atoms in ^{13}C NMR depend on the same effects as the chemical shifts of protons in ^1H NMR.

9. Applications of NMR Spectroscopy

9.1. NMR Investigations for catalyst frameworks

For a number of nuclei, such as ^1H (spin $I = 1/2$, $I_{\text{rel}} = 1$), ^7Li ($I = 3/2$, $I_{\text{rel}} = 0.272$), ^{11}B ($I = 3/2$, $I_{\text{rel}} = 0.133$), ^{23}Na ($I = 3/2$, $I_{\text{rel}} = 9.27 \times 10^{-2}$), ^{27}Al ($I = 5/2$, $I_{\text{rel}} = 0.207$), ^{29}Si ($I = 1/2$, $I_{\text{rel}} = 3.69 \times 10^{-4}$), ^{31}P ($I = 1/2$, $I_{\text{rel}} = 6.65 \times 10^{-2}$), ^{51}V ($I = 7/2$, $I_{\text{rel}} = 0.383$), ^{71}Ga ($I = 3/2$, $I_{\text{rel}} = 5.65 \times 10^{-2}$) and ^{133}Cs ($I = 7/2$, $I_{\text{rel}} = 4.82 \times 10^{-2}$) the investigation of solid catalysts by solid-state NMR spectroscopy using samples with isotopes in natural abundance is a standard characterization. Where the I_{rel} is the relative intensity in comparison with ^1H nuclei having $I_{\text{rel}} = 1$. ^1H nuclei have highest NMR Sensitivity.

Other nuclei, such as ^{13}C ($I = 1/2$, $I_{\text{rel}} = 1.76 \times 10^{-4}$), ^{15}N ($I = 1/2$, $I_{\text{rel}} = 3.85 \times 10^{-6}$) and ^{17}O ($I = 5/2$, $I_{\text{rel}} = 1.08 \times 10^{-5}$) [8], require an isotopic enrichment, making experiments more expensive.

9.2. Solid-State ^{29}Si NMR Spectroscopy of Catalysts

The basic structural units of zeolite catalysts are TO4 tetrahedra with silicon atoms at the central T-positions. In the second coordination sphere of these T-atoms, various metal atoms, such as aluminum, boron, gallium, iron and titanium, can be incorporated into the framework. Depending on the number of metal atoms that are incorporated in the second coordination sphere of T-positions, the tetrahedrally coordinated silicon atoms (Q_4) are characterized by up to five different environments, denoted $\text{Si}(n\text{T})$ with $n = 0, 1, 2, 3$ and 4.

In the case of aluminum atoms incorporated at T-positions, each type of $\text{Si}(n\text{Al})$ species yields a ^{29}Si MAS NMR signal in a well-defined range of chemical shifts. Aluminium atoms are highly important because tetrahedrally co-ordinated Al atoms which are part of lattice generate Bronsted acid sites. On the other hand aluminum oxide clusters inside the zeolites pores may act as Lewis type acid sites and/or may enhance the strength of Bronsted type acid sites. Therefore, it is essential to determine the fraction of framework and non framework aluminum atoms

Aluminum atoms, which are tetrahedrally coordinated and part of the zeolite lattice generate Bronsted type acid sites. On the other hand aluminum oxide clusters inside the zeolites pores may act as Lewis type acid sites and/or may enhance the strength of Bronsted type acid sites. Therefore, it is essential to determine the fraction of framework and nonframework aluminum atoms.

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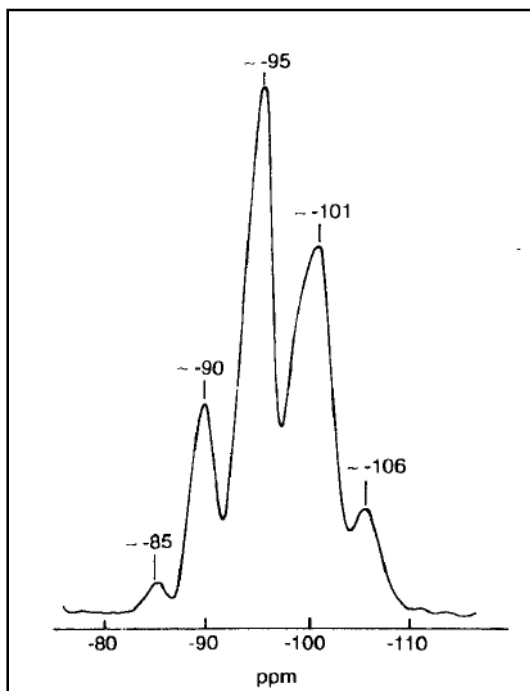
In the ^{29}Si MAS-NMR spectra of zeolites up to 5 well separated peaks are observed, which can be assigned to Si atoms connected via oxygen atoms to other framework atoms such as Si or Al (i.e., $\text{Si}(n\text{Al})$ $n = 0 \dots 4$). For each Al atom in the direct neighborhood to a Si atom a downfield shift of 5 ppm is observed.

According to Lowenstein's rule, each Al atom is surrounded by 4 Si atoms, while the Si atoms can be surrounded by up to four Al atoms.

The relative intensities of the ^{29}Si MAS NMR signals of the $\text{Si}(n\text{Al})$ species are a function of the framework composition. Therefore, the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio of zeolite catalysts can be calculated via

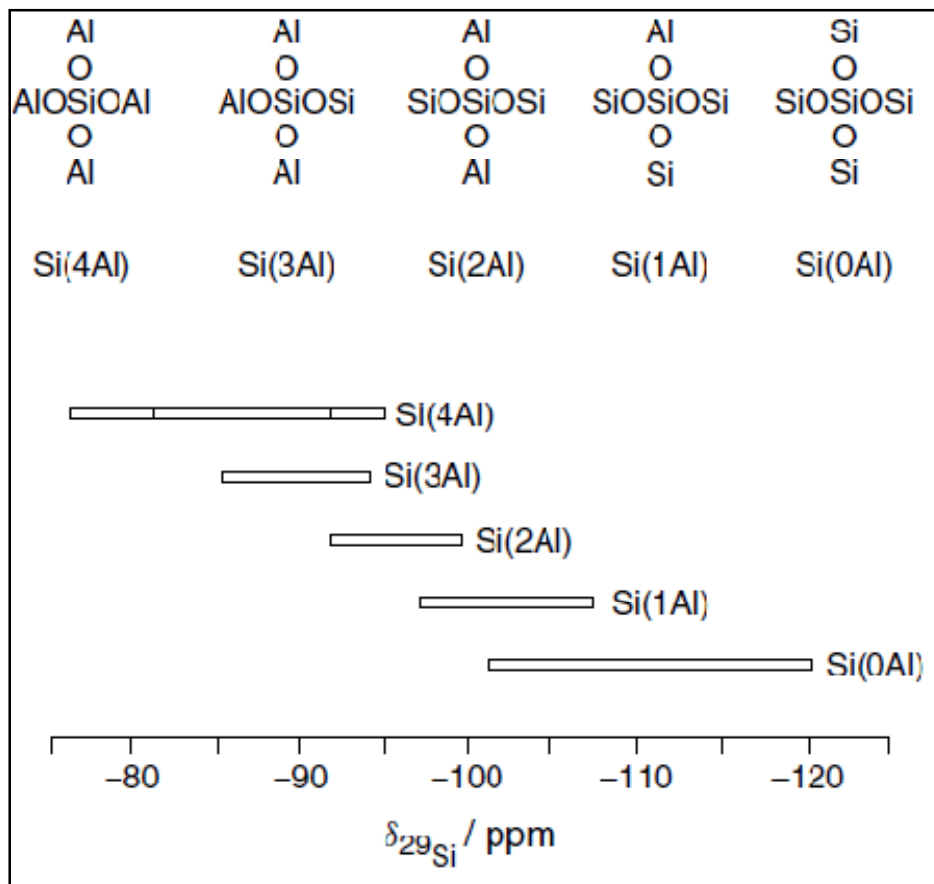
$$\frac{n_{\text{Si}}}{n_{\text{Al}}} = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 0.25n I_{\text{Si}(n\text{Al})}}$$

where $I_{\text{Si}(n\text{Al})}$ is the intensity of the $\text{Si}(n\text{Al})$ signal, i.e. of the NMR signal caused by silicon atoms with n aluminum atoms in the second coordination sphere.



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This method is independent of the zeolite structure and the type of charge balancing cations and includes only A1 atoms that are part of the zeolite lattice. Therefore, NMR yields the framework Si/Al ratio



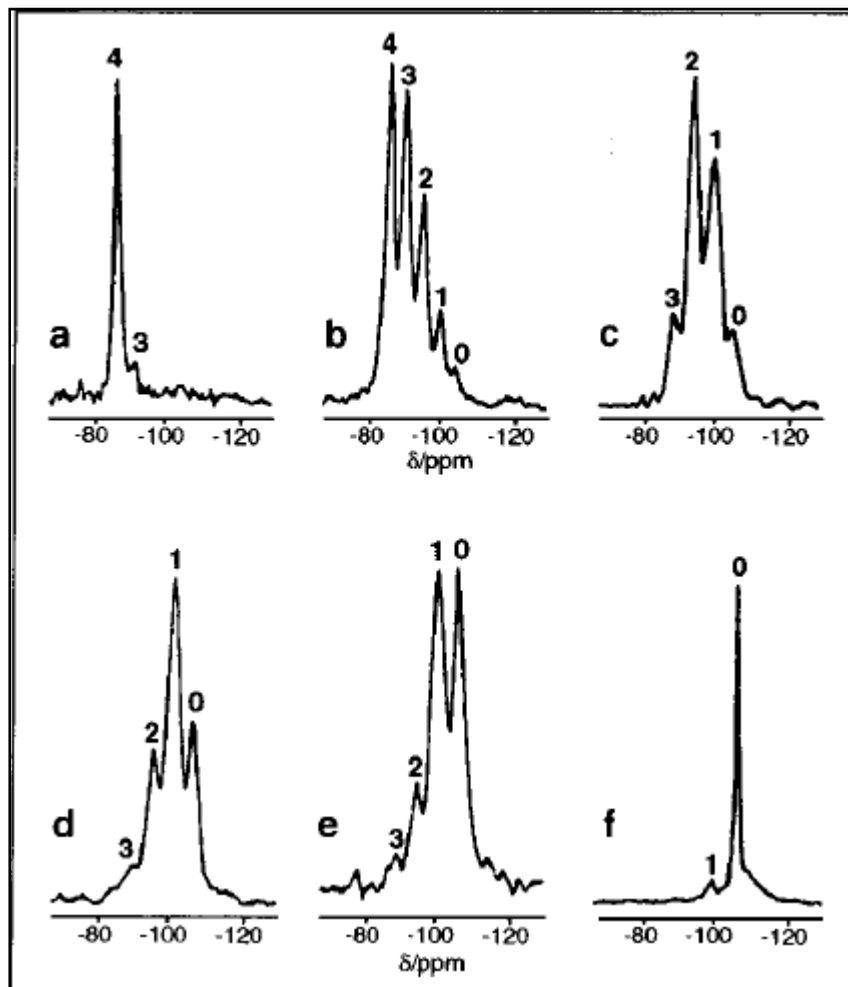
Distinct signals appear in the ^{29}Si NMR spectra of zeolites for the different Si(nAl) environments forming the tetrahedral zeolite framework. The relative signal intensities are directly related to the relative concentrations of the various Si(nAl) units present in the zeolite structure. Following figure shows the ^{29}Si NMR spectra of a series of zeolites X and Y with different Si/Al ratios

With increasing Si/Al ratio, the decrease of the signal intensities of the aluminium-rich Si(nAl) units and a corresponding increase of the aluminium-poor Si(nAl) peaks is clearly visible.

Consequently, from a careful analysis of the chemical shifts and line intensities, the specific types and relative populations of the distinct Si(nAl) units present in a zeolite can, in principle, be determined. Moreover, if other tetrahedral atoms replacing aluminium and/or silicon are present in the framework, characteristic shifts of the Si(nT) lines may be observed.

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Silicon atoms bearing OH groups, e.g. $\text{Si}(\text{OH})(\text{OSi})_3.n(\text{OAl})_n$, located in framework defects or in amorphous parts of the zeolite material exhibit peaks characteristically shifted to low field from the corresponding $\text{Si}(n\text{Al})$ units and may overlap with the $\text{Si}[(n+1)\text{Al}]$ signals.



a - $\text{Si}/\text{Al} = 1.02$ b - 1.41 c - 2.45 d - 3.77 e - 4.88 f - ca 50

Other applications of ^{29}Si NMR Spectroscopy are:

1. The chemical compositions of the framework of the gallium analogue of zeolite Beta, $[\text{Ga}]\text{Beta}$, and of zincosilicates can be obtained.
2. Characterization of zeolites VPI-7 and VPI-7.

In each zeolite catalyst, terminal hydroxyl groups bound to silicon atoms exist [Q3, $\text{Si}(3\text{Si},1\text{OH})$; Q2, $\text{Si}(2\text{Si},2\text{OH})$]. These hydroxyl groups are located at the outer surface

of zeolite particles or at internal framework defects. It is important to note that Si(1Al) species ($\delta^{29}\text{Si} = -95$ to -105 ppm) occur at the same resonance positions as Si(3Si,1OH) species ($\delta^{29}\text{Si} = -100$ to -103 ppm) [46]. A quantitative evaluation of the relative intensities of Si(nT) signals therefore requires the determination of the concentration of Q3 silicon species, which can be performed via quantitative ^1H MAS NMR spectroscopy of the SiOH groups in the dehydrated material

9.3. Solid-State ^{27}Al NMR Spectroscopy of Catalysts

According to Loewenstein's rule, the formation of Al–O–Al bonds in aluminosilicates and aluminophosphates is forbidden, and only Al(4Si) and Al(4P) species can exist in the corresponding frameworks. Therefore, ^{27}Al MAS NMR spectra of hydrated zeolite catalysts and aluminophosphates consist, in general, of only one signal of framework aluminum atoms (Al^{f}) in a range of chemical shifts between ca. 35 and 60 ppm (referenced to a 0.1 M aqueous solution of $\text{Al}(\text{NO}_3)_3$ in D_2O). In hydrated aluminosilicates and aluminophosphates, only small deviations from the ideal tetrahedral symmetry of the AlO_4 units occur, which lead to weak quadrupolar interactions and weak second-order quadrupolar line broadenings.

Extra-framework aluminum (Al^{nf}) species in hydrated zeolites, formed e.g. as a result of calcination and steaming, are octahedrally coordinated AlO_6 species and cause ^{27}Al NMR signals at -15 to 0 ppm.

If extra-framework aluminum exists as polymeric aluminum oxide or oxide hydrates in zeolite cages or channels, a strong second-order quadrupolar line broadening may occur owing to distortions of the octahedral symmetry of these AlO_6 species. In some cases, an additional broad signal occurs at 30 – 50 ppm, which is caused by aluminum atoms in a disturbed tetrahedral coordination or a pentacoordinated state.

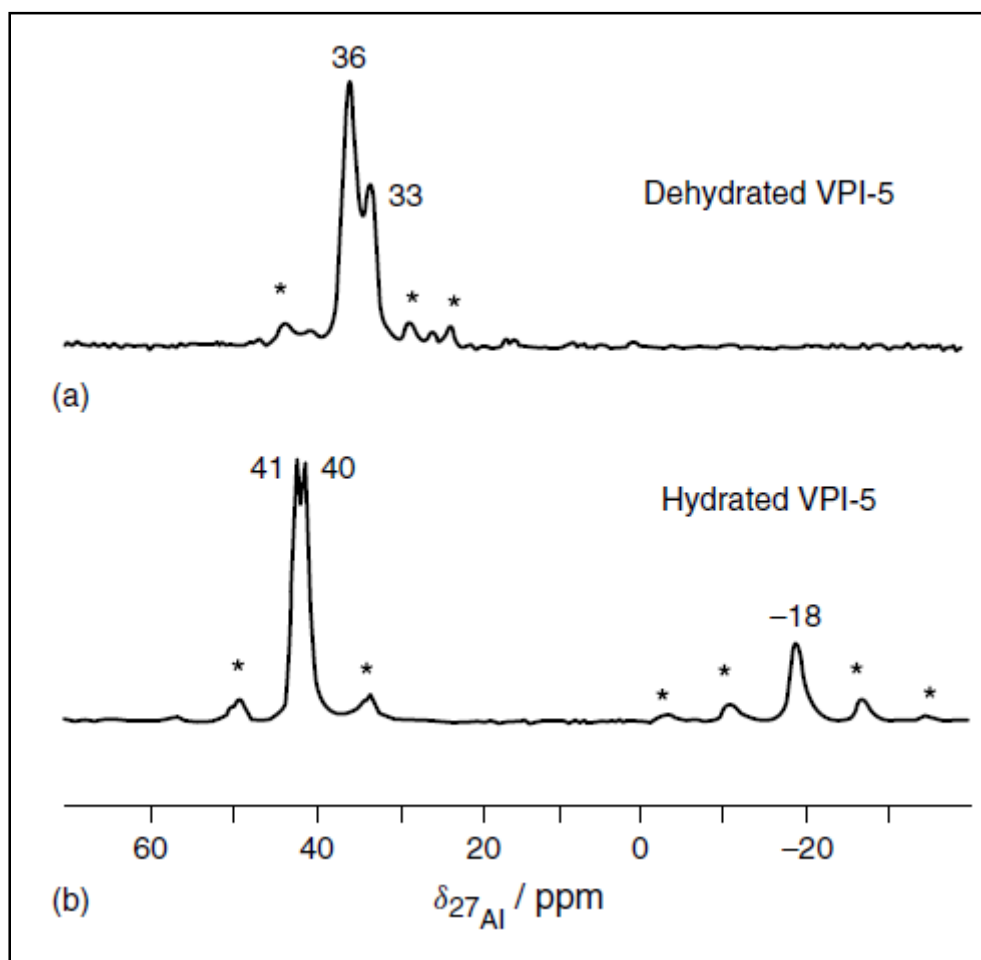
For the ^{27}Al MAS NMR signals of tetrahedrally coordinated framework aluminum atoms, no definite relationships were found between the chemical shift, $\delta^{27}\text{Al}$ and the $n\text{Si}/n\text{Al}$ ratio or the Si–Al order scheme of the zeolite framework. However, by ^{27}Al and ^{29}Si MAS NMR spectroscopy of lithium and sodium halide aluminosilicate sodalites with high-speed sample spinning, Jacobsen et al. obtained the following linear correlation between the ^{27}Al NMR shift, $\delta^{27}\text{Al}$ and the ^{29}Si NMR shift, $\delta^{29}\text{Si}$, of aluminum and silicon atoms, respectively

$$\frac{\delta^{27}\text{Al}}{\text{ppm}} = \frac{1.03\delta^{29}\text{Si}}{\text{ppm}} + 151.94$$

NMR Spectroscopy

Whereas the MAS technique reduces the second-order quadrupolar line broadening by a factor of only ca. 3.6, application of the DOR technique results in a complete averaging of this interaction.

Crystalline aluminophosphates are materials with a high degree of framework ordering. The framework of aluminophosphates is built of AlO_4 and PO_4 tetrahedra in an alternating arrangement. The ^{27}Al DOR NMR spectra of these materials consist of narrow signals due to aluminum atoms at crystallographically non-equivalent T-sites or caused by framework aluminum atoms interacting with probe molecules.



The ^{27}Al DOR NMR spectrum of the dehydrated aluminophosphate VPI-5 is shown. It consists of two signals at 36 and 33 ppm with an intensity ratio of 2 : 1.

Addition of water molecules dramatically alters the local bonding of the framework aluminum atoms in VPI-5. The lines at 36 and 33 ppm have disappeared, and two partially resolved signals associated with tetrahedrally coordinated framework aluminum atoms are present at 41 and 40 ppm. In addition, a high-field signal occurs at

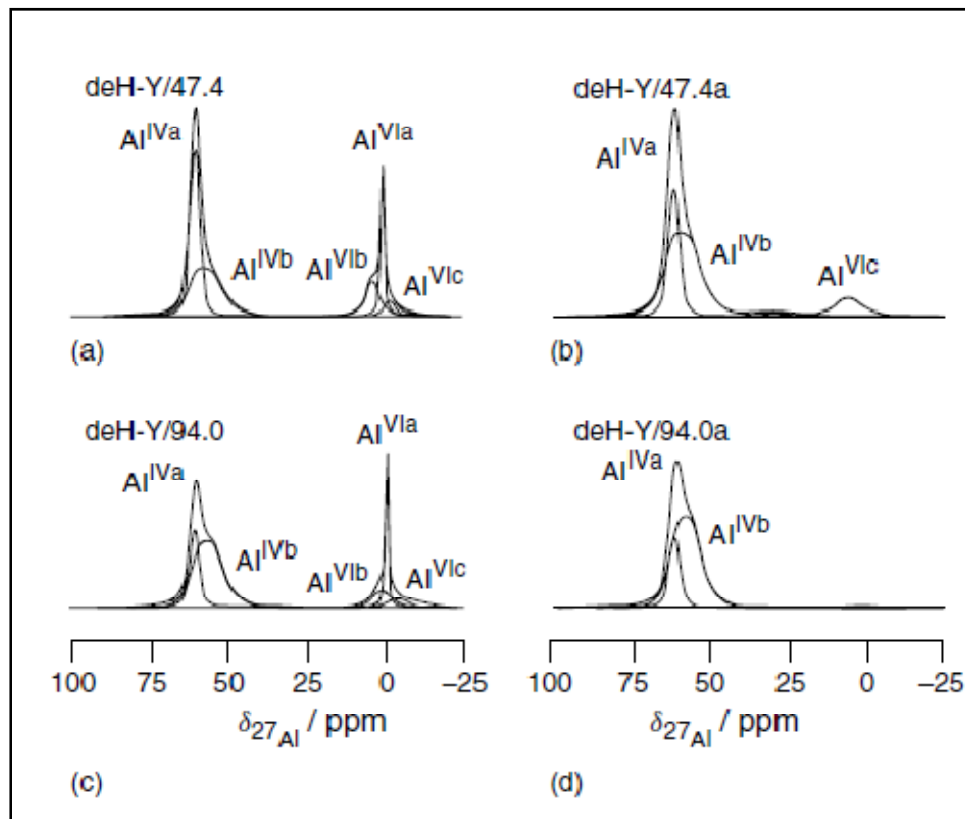
NMR Spectroscopy

-18 ppm in the range ascribed to octahedrally coordinated aluminum species.

Wouters et al. suggested partial hydrolysis of framework Al-O bonds and a generation of framework-connected AlOH groups upon calcination or steaming of zeolite catalysts. In a second step, these framework aluminum atoms coordinate to water molecules, giving rise to octahedrally coordinated framework aluminum species. Subsequent adsorption of ammonia on the material converts the Al^{VI} atoms back to Al^{IV} atoms. The ammonia-induced coordination change of aluminum atoms in zeolites was investigated by high-field ²⁷Al MAS NMR and ²⁷Al MQMAS NMR spectroscopy.

Following figure shows high-field ²⁷Al MAS NMR spectra of zeolites H-Y steamed at 753 K for 2.5 h at a water vapor pressure of 47.4 kPa (deH-Y/47.4) and 94.0 kPa (deH-Y/94.0). In addition, the latter sample was washed in 0.1 M HCl after steaming. Before recording the spectra on the right-hand side, adsorption of ammonia at a pressure of 5 kPa for 1.5 h on the dehydrated samples was performed on both samples. Upon rehydration, it was found that Al^{VIa} and Al^{VIb} species are involved in a coordination change from Al^{VI} to Al^{IV}.

By ²⁷Al MQMAS NMR spectroscopy, a quadrupolar coupling constant of $C_{\text{QCC}} = 2-3$ MHz (typical for framework aluminum atoms) was determined for the Al^{VIa} and Al^{VIb} atoms. The Al^{VIc} atoms, which were not involved in the ammonia-induced coordination change, cause an ²⁷Al MQMAS NMR signal with a CQCC value of ca. 5 MHz. This large quadrupolar coupling constant indicates that the corresponding Al^{VI} atoms are due to aluminum species in extra-framework clusters. Washing the sample with HCl leads to preferential removal of Al^{VIc} atoms.



SEDOR and REDOR experiments are suitable for the determination of the bonding geometries of aluminum atoms in solid catalysts.

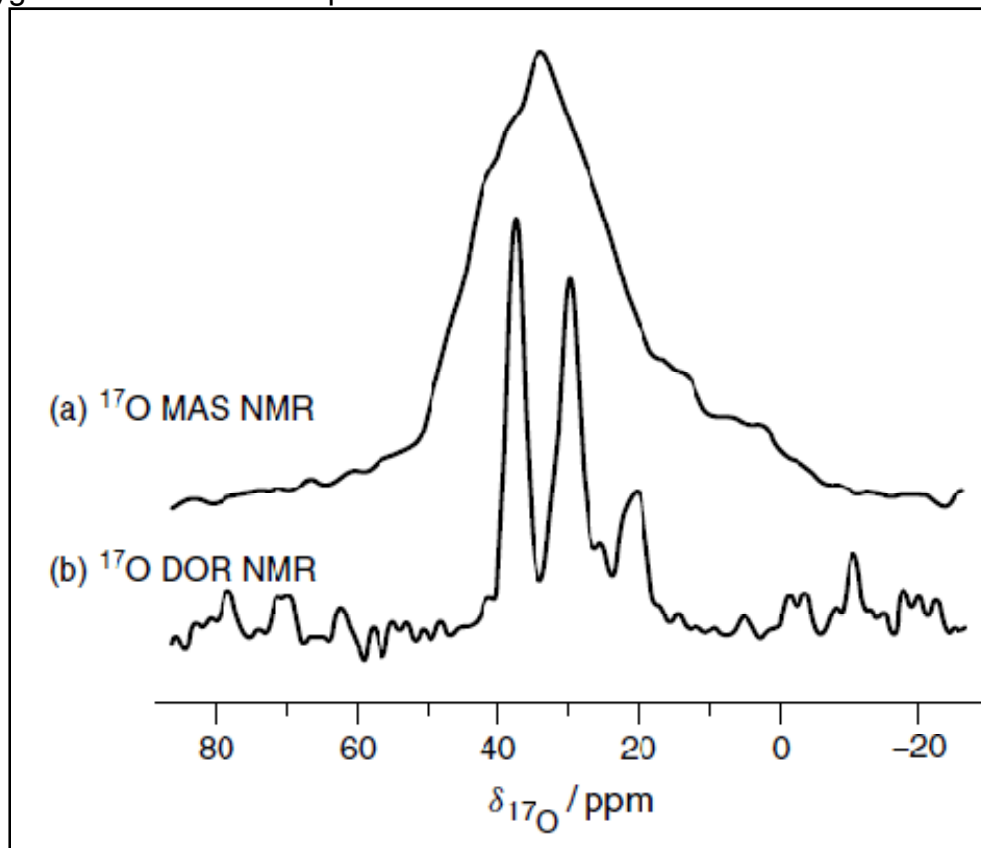
9.4. Solid-State ^{17}O NMR Spectroscopy of Catalysts

Due to the low natural abundance of ^{17}O nuclei of 0.037%, ^{17}O NMR spectroscopy of solid catalysts requires an isotopic enrichment. This enrichment can be performed by, e.g., treatment of the powder material in a reactor with H_2^{17}O vapor at 523 K for some hours.

Nowadays, solid-state ^{17}O NMR investigations of catalysts are performed applying the DOR and MQMAS technique. For obtaining above spectra ordered local structures should be present. In this case the different signals of ^{17}O nuclei appear at crystallographically non-equivalent positions as well as resolved lines also appear in DOR and MQMAS spectrum. Pingel et al. investigated zeolites Na-A and Na-LSX ($n_{\text{Si}}/n_{\text{Al}} = 1$) with ^{17}O DOR and MQMAS NMR spectroscopy. Whereas the ^{17}O MAS NMR spectrum of zeolite Na-LSX ($n_{\text{Si}}/n_{\text{Al}} = 1$) consists of a single broad signal, application of the DOR technique leads to splitting of the spectrum into three different signals.

NMR Spectroscopy

Structure of zeolite X is characterized by four crystallographically non-equivalent oxygen positions. Therefore the peak at the middle must be due to the superposition of two signals of oxygen atoms at different positions.



9.5. NMR Investigations of Heterogeneously Catalyzed Reactions

1. H-D Exchange between Adsorbate Molecules and Solid Acid Catalysts

Investigated by In Situ ^1H and ^2H MAS NMR Spectroscopy Under Batch Conditions

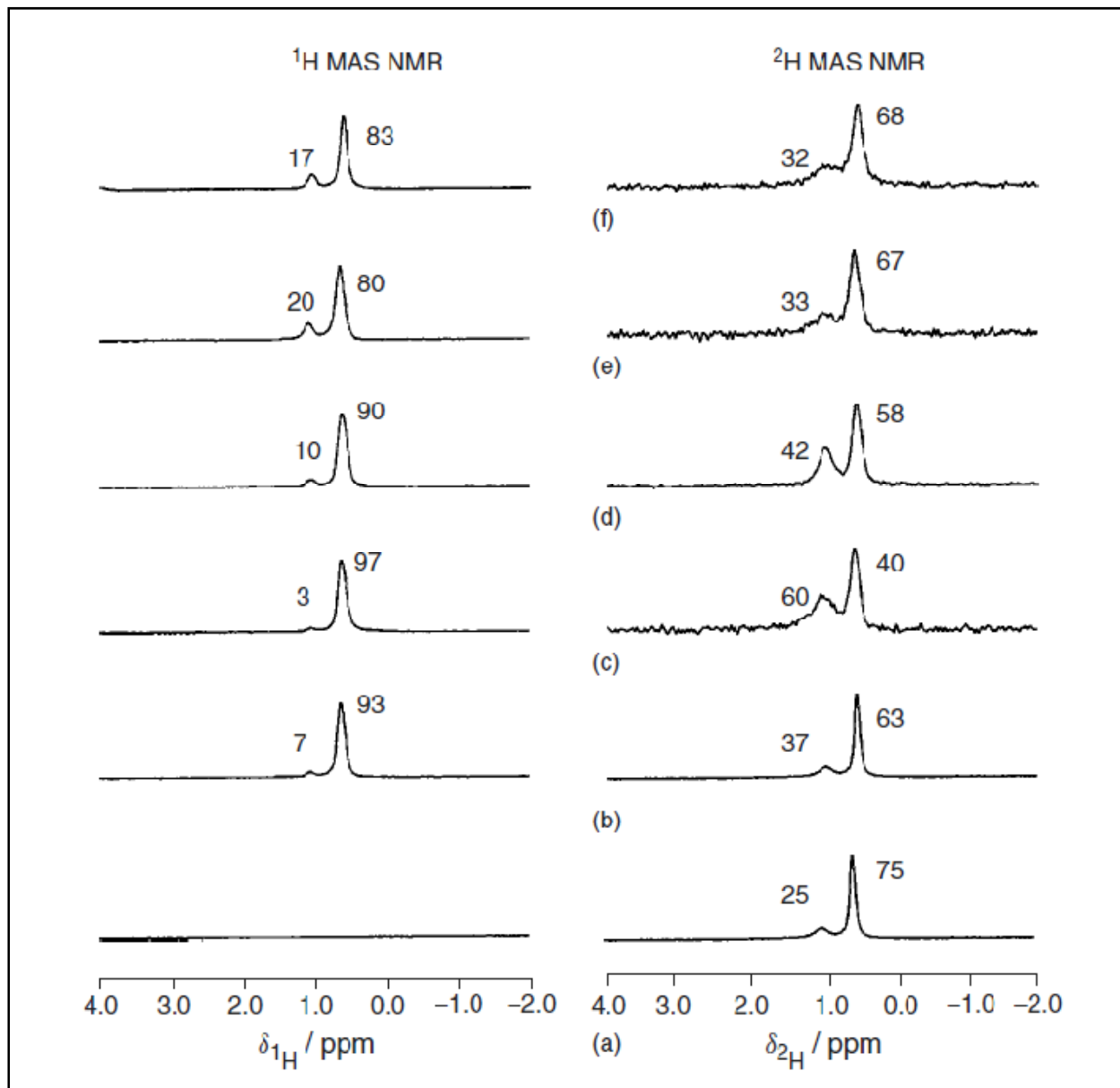
H-D isotope exchange between hydroxyl groups of solid acid catalysts and adsorbate molecules can provide valuable information, not only for evaluating the acid strength of the hydroxyl groups, but also for studying the mechanisms of heterogeneously catalyzed reactions on these solid acids. Characterization of the surface acidity of solid acids by studying the H-D exchange can be achieved by ^1H MAS NMR spectroscopy

NMR Spectroscopy

Haouas et al. applied in situ MAS NMR spectroscopy to investigate the initial stage of propane activation on Al₂O₃-promoted sulfated zirconia (SZA) within the low-temperature range 303–375 K. The intramolecular hydrogen scrambling of propane was further investigated by ¹H and ²H NMR spectroscopy. Following figure shows the ¹H and ²H MAS NMR spectra of propane-d₈ adsorbed on Al₂O₃-promoted SZA after longer contact times at different temperatures.

The ²H NMR spectrum (right) obtained before heating consists of signals of CD₃ (0.5 ppm) and CD₂ (1.0 ppm) groups in an intensity ratio of 3 : 1. In the ¹H MAS NMR spectrum (left), no signals occur. After starting the reaction, a substantial decrease of the ²H MAS NMR signal intensity can be observed with a CD_yH_(3-y):CD_xH_(2-x) ratio below 3. While the ¹H MAS NMR spectra have corresponding signals in a ratio much larger than 3 at all temperatures (left).

NMR Spectroscopy



(a) before reaction and after, (b) 50 h at 303 K, (c) 25 h at 321 K, (d) 25 h at 335 K, (e) 16 h at 344 K and (f) 8 h at 355 K.

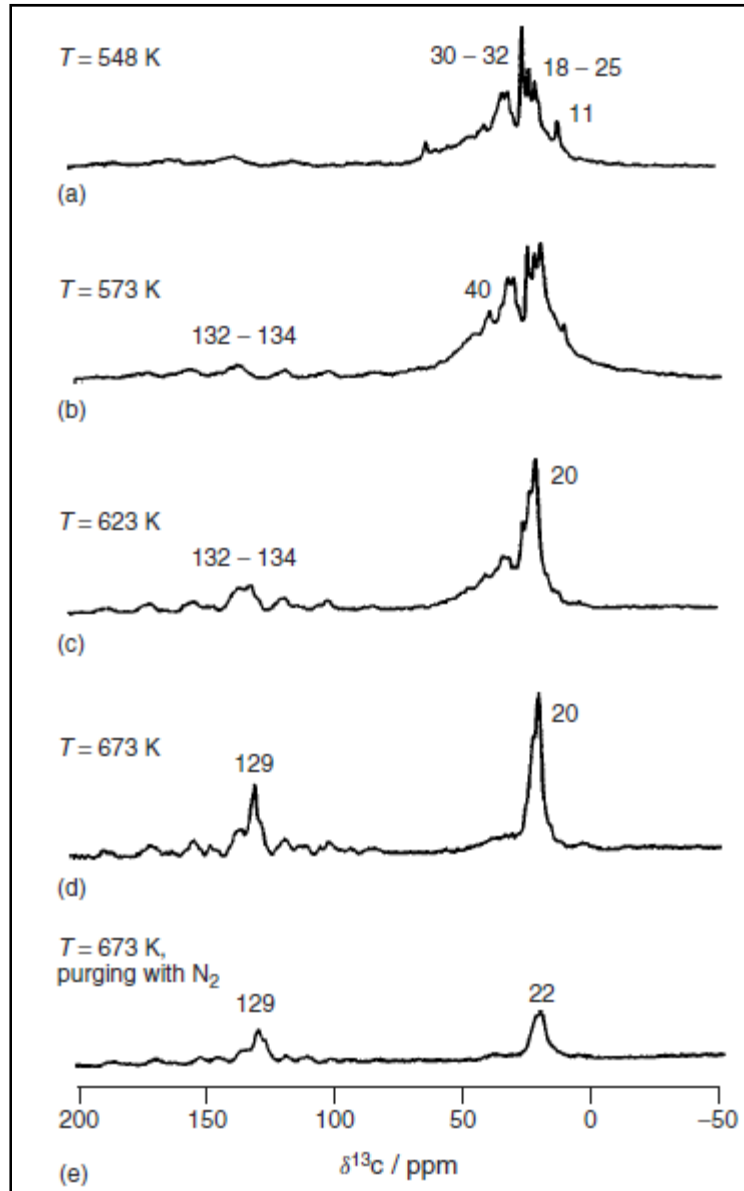
This finding agrees with a rapid H-D exchange between methyl groups and the solid catalyst and indicates that an intramolecular H-D scrambling between methyl and methylene hydrogen atoms of propane molecules occurs at higher temperatures. Additionally, an intramolecular ^{13}C scrambling by a skeletal rearrangement process is favored at higher temperatures, which was monitored by ^{13}C MAS NMR spectroscopy.

2. Methanol-to-Olefins (MTO) reaction on Acidic Zeolite Catalysts:

The in situ MAS NMR technique under continuous flow (CF) conditions allows a direct NMR investigation of the formation and transformation of surface species and a simultaneous gas chromatographic analysis of the reaction products under steady-state conditions. To investigate methanol conversion under steady-state conditions by in situ ^{13}C CF MAS NMR spectroscopy, a flow of ^{13}C -enriched methanol ($^{13}\text{CH}_3\text{OH}$) was continuously injected into a spinning MAS NMR rotor reactor filled with the calcined zeolite catalyst.

Following figure shows the in-situ ^{13}C CF MAS NMR spectra obtained during the conversion of $^{13}\text{CH}_3\text{OH}$ on H-SAPO-34 at reaction temperatures of 548–673 K. The formation of hydrocarbons on the working catalyst was evidenced by the ^{13}C MAS NMR signals appearing in the alkyl region of 10–40 ppm accompanied by broad signals in the olefinic and aromatic region of 129–134 ppm. It was found through deconvolution of the spectra that the hydrocarbon pool species on the working catalyst under steady-state conditions consist of a mixture of C6 –C12 aromatics and olefins, such as hexenes, hexadienes and polymethylbenzenes. To study the organic species occluded in H-SAPO-34 after methanol conversion, the working catalyst was further purged with dry carrier gas (nitrogen) at 673 K. The spectrum obtained after purging consists of signals at 22 and 129 ppm, indicating the presence of alkylated aromatic compounds occluded in the cages of H-SAPO-34.

NMR Spectroscopy



9.6. NMR Spectroscopy for the Characterization of Surface Acidity and Basicity

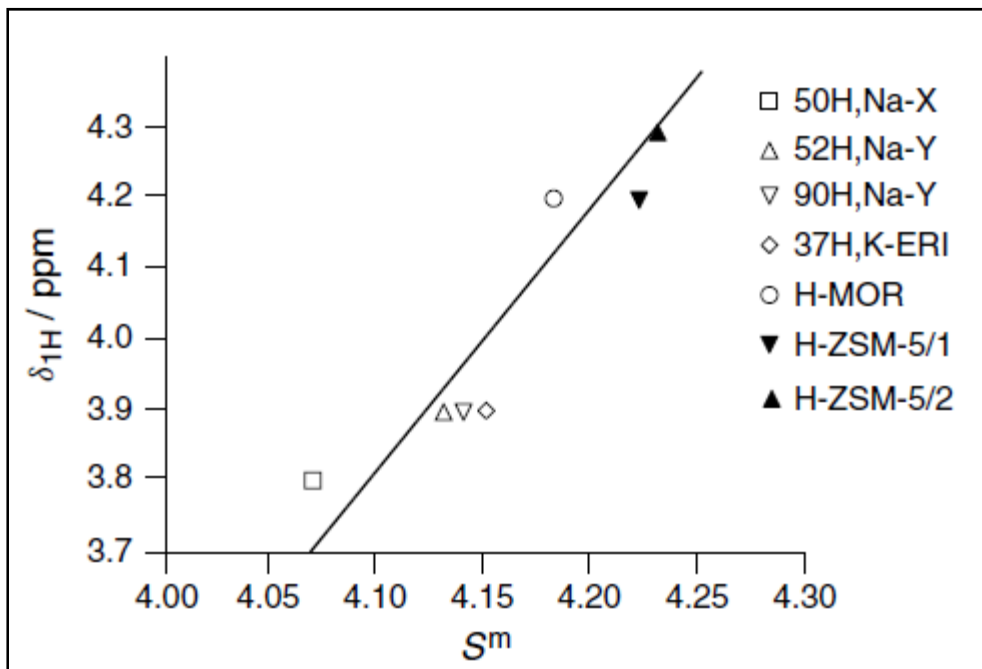
Characterization of Brønsted acid sites, Lewis acid sites and base sites can be done. Solid state NMR spectroscopy allows the determination of the type, strength, accessibility and concentration of surface sites.

1. Investigation of Brønsted Acidic Hydroxyl Groups by ^1H MAS NMR Spectroscopy

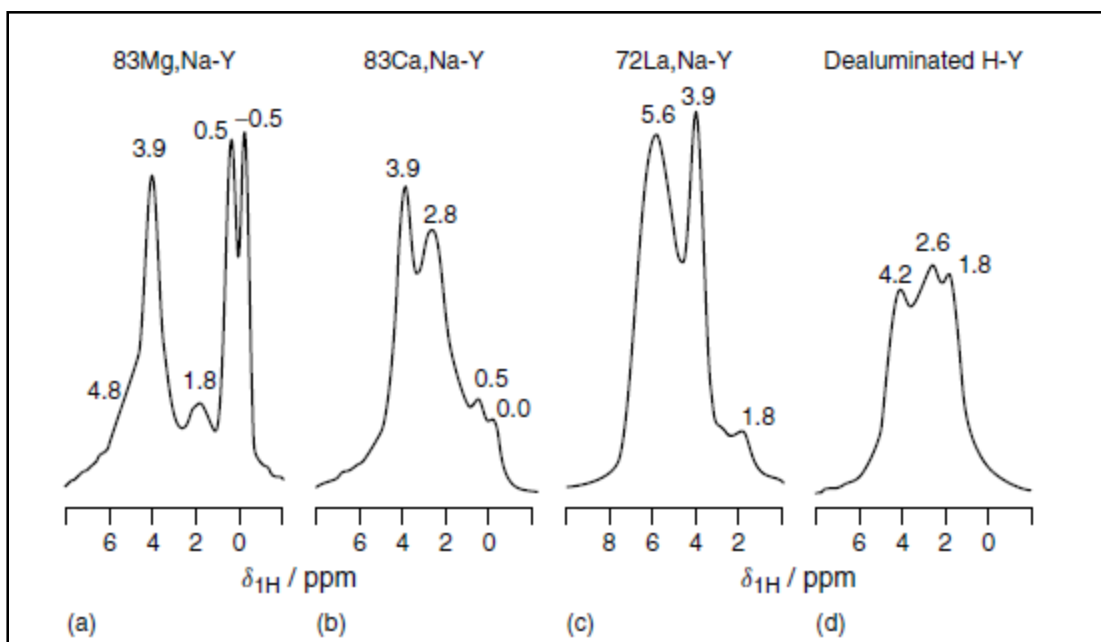
^1H MAS NMR signals of hydroxyl groups in calcined solid catalysts cover a range of isotropic chemical shifts from $\delta^1\text{H} = 0$ to ca. 15 ppm.

^1H NMR shift, $\delta^1\text{H}/\text{ppm}$	Abbreviation	Type of hydroxyl group
-0.5 to 0.5	MeOH	Metal or cation OH groups in large cavities or at the outer surface of particles
1.2–2.2	SiOH	Silanol groups at the external surface or at lattice defects
2.4–3.6	AlOH	OH groups bonded to extra-framework aluminum species located in cavities or channels involved in hydrogen bonding
2.8–6.2	CaOH', AlOH', LaOH'	Cation OH groups located in sodalite cages of zeolite Y and in channels of ZSM-5 involved in hydrogen bonding
3.6–4.3	SiOHAl	Bridging OH groups in large cavities or channels of zeolites
4.6–5.2	SiOH'Al	Bridging OH groups in small channels and cages of zeolites
5.2–8.0	SiOH'Al	Perturbed bridging OH groups in zeolites H-ZSM-5, H-Beta and MCM-22
ca. 15	SiOH'	Internal SiOH groups involved in strong hydrogen bonding

NMR Spectroscopy



Above curve indicates that chemical shift increases with the decrease in framework aluminium content or increasing mean electronegativity of framework. Therefore this can be correlated to the increase in acid strength of the surface sites. However this may not be applicable in cases where steric effects dominate.



Typical 1H MAS NMR spectra of dehydrated zeolites Y are shown in above figure. The spectrum of zeolite 83Mg,Na-Y consists of signals of MgOH groups at

-0.5 and 0.5 ppm, silanol groups at 1.8 ppm and bridging OH groups in the supercages and in the sodalite cages at 3.9 and 4.8 ppm, respectively (Fig. a). In the spectrum of zeolite $^{83}\text{Ca},\text{Na}-\text{Y}$, a signal due to CaOH groups in the sodalite cages occurs at 2.8 ppm (Fig. b). Lanthanum hydroxyl groups of lanthanum cations and oxide complexes located in the sodalite cages cause a signal at 5.6 ppm in the spectrum of zeolite $^{72}\text{La},\text{Na}-\text{Y}$ (Fig. c). The dealumination of zeolite H-Y is accompanied by the formation of hydroxyl groups at extra-framework aluminum complexes leading to a signal at ca. 2.6 ppm in Fig. d. The decrease of the framework aluminum content due to dealumination causes an increase of the mean framework electronegativity and, therefore, a shift of the signal of unperturbed bridging OH groups in the supercages from 3.9 ppm for the parent zeolite H-Y to 4.2 ppm for the dealuminated material (Fig. d).

2. Investigation of accessibility and strength of Brønsted Acid sites using NMR:

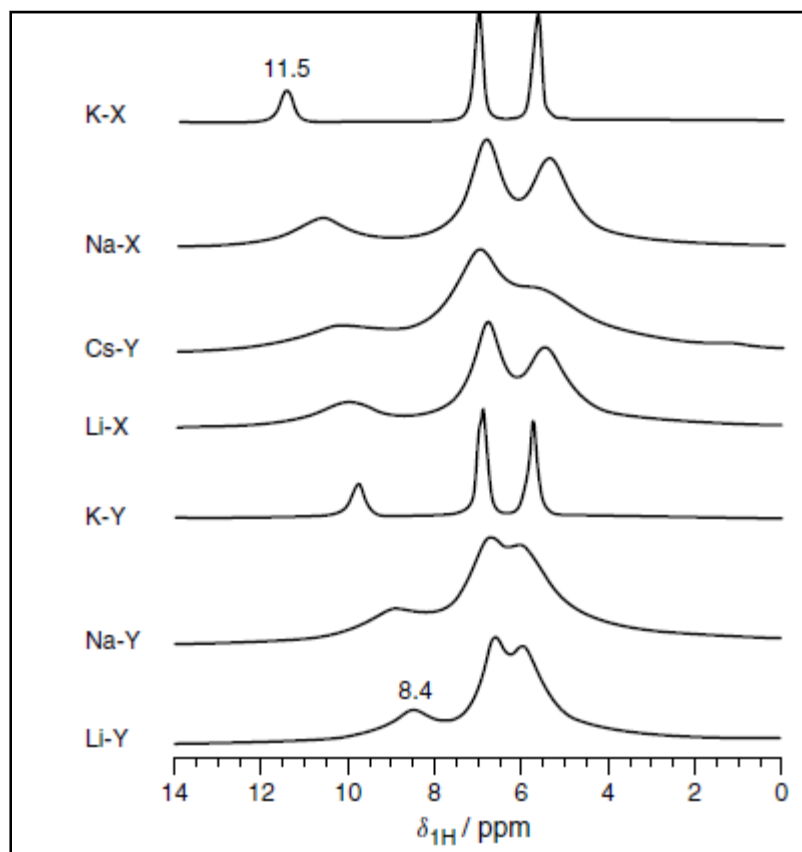
- ✓ Involves application of probe molecules with different sizes and base strengths.
- ✓ Sometimes reactants of heterogeneously catalysed reactions are used as probe molecules.
- ✓ The ability to protonate strongly basic probe molecules, such as pyridine or trimethylphosphine, or to form hydrogen bonds to these molecules is utilized to distinguish between acidic and non-acidic sites.
- ✓ For more quantitative comparison of acid strengths of Brønsted acid sites is possible with weakly basic probe molecules such as acetonitrile and acetone etc.
- ✓ Adsorption of pyridine is useful for distinguishing acidic from non-acidic OH groups.
- ✓ A frequently applied probe molecule for characterizing the strength of Brønsted acid sites in solid catalysts in a more quantitative manner is $[2-^{13}\text{C}]\text{acetone}$

3. Solid-State NMR Investigations of Lewis Acid Sites by Probe Molecules

- ✓ Techniques such as DOR and MQMAS can be used.
- ✓ Hydration of activated solid catalysts is accompanied by strong modification of the surface sites.
- ✓ Therefore the investigation of Lewis acid site requires the probe molecules.
- ✓ Probe molecules such as TCM, TFM, Pyrrole, chloroform can be used.

NMR Spectroscopy

- ✓ In the presence of lewis acid sites various complexes are formed by coordination of probe molecules at this site and are available for solid state NMR spectroscopy.
 - ✓ However so far no correlation between the NMR shift of probe molecules coordinated to lewis acid sites and the strength of surface sites has been found.
4. **Solid-State NMR Investigations of Base Sites in Solid Catalysts**
- ✓ Due to advances in NMR spectroscopy solid state ^{17}O NMR spectroscopy became a suitable method of direct investigation of basic oxygen atoms in zeolite catalysts.
 - ✓ Probe molecules such as Trichloro and Trifluoromethane can be used.



Above figure shows ^1H MASNMR spectra of pyrrole adsorbed on various alkali metal-exchanged zeolites X and Y. The hydrogen atoms at the rings of the pyrrole molecules are not influenced by the different zeolites and cause the two signals at 6–7 ppm.

NMR Spectroscopy

The ^1H NMR shift of the hydrogen atoms at the ring nitrogens, however, covers a range between 8.4 (Li-Y) and 11.5 ppm (K-X) and indicates the different base strengths of zeolite oxygen atoms contributing to the hydrogen bondings with the pyrrole molecules.

Stronger low field shift corresponds to a higher basic strength. Pyrrole has remarkable sensitivity and good resolution for ^1H spectra.

10. Conclusion:

Due to the development of new techniques and the further increase in the magnetic field strength available for commercial applications, solid-state NMR spectroscopy has become a routine method for the characterization of solid catalysts in recent decades. As an important advantage, solid-state NMR spectroscopy allows the investigation of the local structure of the nuclei under study in both crystalline and amorphous materials. Active sites in solid catalysts and the specific behavior of the frameworks of these materials often depend on local effects, such as framework defects, the substitution of framework atoms, guest compounds, etc. Therefore, solid-state NMR spectroscopy is nowadays a widely applied analytical method delivering information about solid catalysts, which are complementary to those obtained by other analytical methods.

Whereas in early solid-state NMR spectroscopic studies in the field of heterogeneous catalysis the characterization of the catalyst framework was the dominant application, an increasing number of recent studies have focused on the investigation of surface sites, i.e. on the determination of their concentration, strength and accessibility. In this case, the advantage of NMR spectroscopy as a quantitative method can be utilized.

New developments are the different ex situ and in situ techniques used to clarify the interaction of probe molecules and reactants with active surface sites on solid catalysts. Furthermore, some of these approaches are suitable for investigating the mechanisms of heterogeneously catalyzed reactions under conditions that are relevant for industrial processes.

References:

1. Handbook Of Heterogeneous Catalysis, Gerhard Ertl, Helmuth Knözinger
2. Introduction to Zeolite Science and practice, Studies in Surface Science and Catalysis