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Characterization Techniques

Important parameters of catalysts, such as texture and chemical surface, are determinant to be able to relate their catalytic activity to their properties. Thus, characterization of catalysts becomes a key point in any study in the field of catalysis. In the following chapter, several techniques and the experimental conditions used are described in a general way.

2.2.1 Scanning Electron Microscopy (SEM) and X-Ray Microanalysis

External morphology of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (μm) scale can be observed and characterized by scanning electron microscopy (SEM), obtaining magnified three-dimensional-like images of their surfaces.

An extremely fine beam of electrons is directed at the specimen, scanning across the specimen by the scan coils. Three types of electronic signals can be emitted from the surface of the specimen exposed to the incident beam: *backscattered electrons* which possess energy close to that of the incident beam, *secondary electrons* which have a kinetic energy less than 50 eV and *Auger electrons* produce by de-excitation of atoms. The de-excitation of atoms also produces a photon within an emission domain in the range of x-ray to visible. X-rays are used primarily for chemical analysis rather than imaging. The detector collects and converts the radiation of interest that leaves the specimen into an electrical signal for manipulation and display by the signal processing electronics to create an image. The two major parts of a microscope are shown in Fig. 2.2.1.

X-ray spectrum emitted by any specimen allows carrying out a *qualitative* measurement (measuring the wavelength of each emitted X-ray which is characteristic of each element) and a *quantitative* measurement (measuring how many X-ray of any type are emitted per second should tell how much of the element is present).

Experimental Conditions

The measurements were carried out in a JEOL JSM6400 scanning microscope operating at an accelerating voltage in the 15–20 kV range.
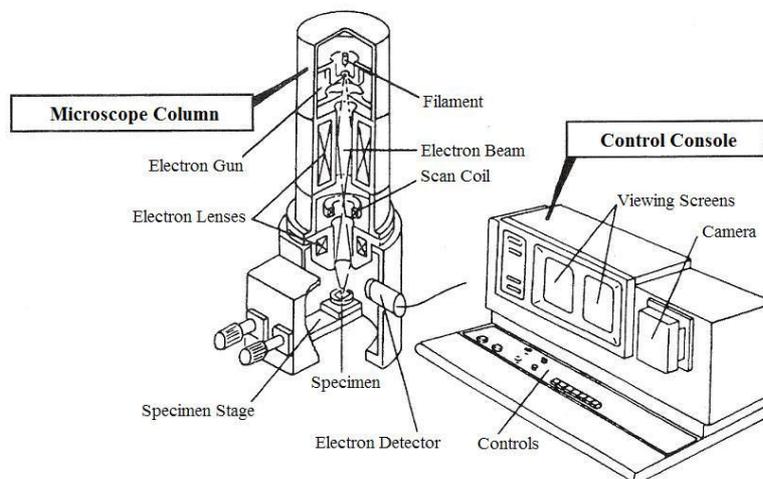
Figure 2.2.1 The two major parts of the SEM, the electron column and the electronics console.

The specimen support used for mounting samples consisted of aluminium alloy-stub. One side of the stub was covered by a double sided- adhesive carbon tape, where the specimen was set. If the specimen was non-conductive, a thin coating layer of gold was applied by sputtering [1-3].

2.2.2   Transmission Electron Microscopy (TEM)

The internal structure of solids and their microstructural and ultrastructural detail are able to be probed by transmission electron microscopy (TEM), which gives to this technique a wide application field in heterogeneous catalysis.

The formation of images is very similar to than in an optical microscope, but it uses electrons instead of light. An electron gun at the top of the microscope (Fig. 2.2.2) emits the electrons that travel through vacuum in the column of the microscope. The acceleration voltage is commonly 100-200 kV, although higher voltages are also available in some commercial microscopes. A system of condenser lenses demagnifies the beam emitted by the gun and controls its diameter as it hits the specimen. The specimen should be thin enough to transmit the electron beam. The objective lenses form an intermediate magnified image, which is enlarged by the

subsequent projector lenses on a fluorescent screen. The image can be visualized by the operator or photographed with a camera [2-5].

Experimental Conditions

The measurements were performed in a JEOL JEM-2000EX II microscope operated at 80-200 kV. The solid sample, which was homogeneously dispersed in pure acetone by means of an ultrasonic bath, was deposited in the copper grid and then the solvent was allowed to evaporate under vacuum before analysis.
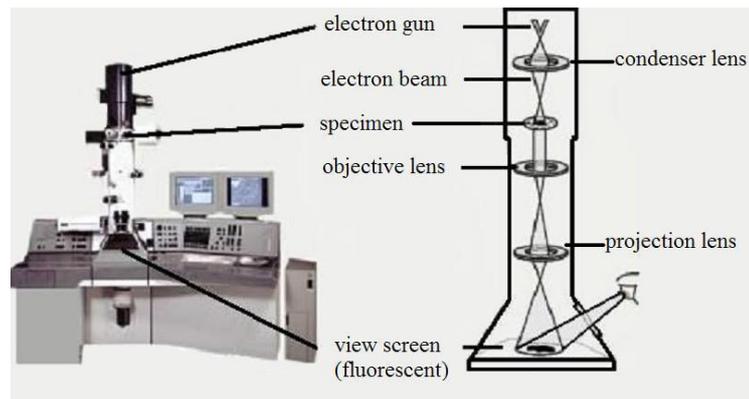

Figure 2.2.2 A modern transmission electron microscope with a schematic representation of the essential parts.

2.2.3   X-Ray Powder Diffraction (XRD)

X-ray powder diffraction plays a critical role in material research and development. Among its applications is the identification of the present phases in a specimen, the quantitative analysis of the concentrations of each phase present in a multiphase specimen, the unit cell metrics, microstructure analysis of polycrystalline materials, etc.

X-rays are diffracted by the crystals. This diffraction represents the interference between X-ray scattered by the electrons in the various atoms at different locations in the unit cell. The diffracted beam is 'reflected' from a plane passing through points of the crystal lattice in a manner that makes this crystal-lattice planes analogous to mirrors, so the angle of incidence is equal to the angle of reflection. The diffraction from a crystal is described by the equation known as Bragg's law:

$$n\lambda = 2\mathbf{d}_{hkl} \sin \theta_{hkl}$$

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Therefore, if λ (x-ray wavelength) and θ_{hkl} (one-half the diffraction angle) are known, then the perpendicular spacing between lattice planes $\mathbf{d}_{hkl}$ and consequently, the unit cells dimensions and the indices *h, k, l* of those crystal planes, can be determined. A powder pattern contains a set of diffraction peaks at 2θ positions which correspond to the interplanar spacing in the crystal. A schematic of x-ray powder diffractometer is shown in Fig. 2.2.3 [6, 7].
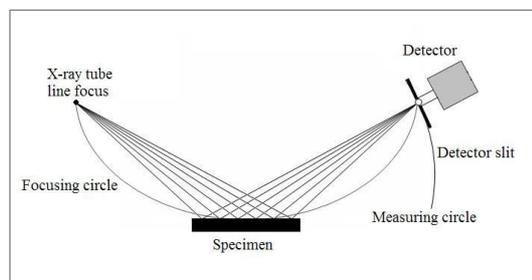

Figure   2.2.3   Schematics   of   a   x-ray   powder diffractometer with a Bragg-Brentano parafocusing geometry.

Experimental Conditions

X-ray powder diffraction patterns of our samples were collected in a Siemens D5000 diffractometer with Bragg–Brentano geometry using nickel-filtered Cu-Kα radiation (λ= 0.15406 nm). Data were collected in the 2θ range of 10-70 degrees with an angular step of 0.058 at 3 s per step. The crystalline phases were identified by using the diffraction patterns of Joint Committee on Powder Diffraction Standards (JCPDS) of the International Centre for Diffraction Data (ICDD).

2.2.4   Fourier-transform Infrared Spectroscopy (FTIR)

One of the principal uses of Fourier-transform infrared spectroscopy (FTIR) is the identification of unknown substances or their characterization as their chemical structure. A spectrum of a material is its fingerprint. Sometimes it is not possible to totally identify a material from its spectrum, but the presence or absence of certain groups can be correlated with the presence or absence of absorption at specific wavelengths.

IR spectroscopy refers to radiation between two vibration states, whose wavelength (λ) is in the range 30 to 3μ ($1\mu=10^{-3}$mm) of the electromagnetic spectrum and the energy differences are in the range between 1-10 kcal mol^{-1}. The

IR spectra usually present a plot of absorption (% of transmission) as a function of wavelength (cm^{-1}).

FTIR spectroscopy is an interferometric method. It is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a irradiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation. A schematic representation of FTIR spectrometer is presented in Fig. 2.2.4 [4, 6, 8].
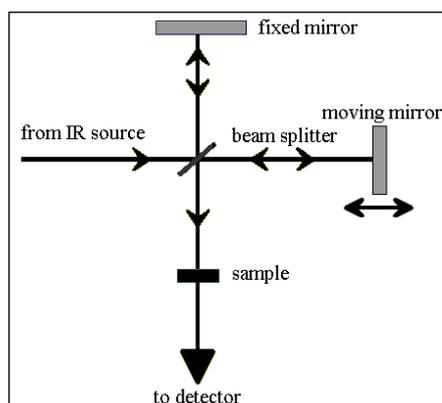

Figure 2.2.4 Schematic set-up of a FTIR spectrometer.

Experimental Conditions

The system used was a Bruker EQUINOX-55 spectrometer supplied with a Pyrex cell with a window of CaF_2. The spectra were obtained directly at room temperature.

2.2.5   Physisorption of Nitrogen

Adsorption occurs whenever a solid surface is exposed to fluid. It means the enrichment of one or more components in an interfacial layer. Particularly, gas adsorption has become a wide-used procedure to determine the surface area and the pore size distribution of porous materials and powders. Porous solids are those solids with cavities or channels which are deeper than they are wide. The pores are arbitrarily classify depending on their diameter width in *micropores* (<20 Å), *mesopores* (200-500 Å) and *macropores* (>500 Å).

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Physisorption is a general phenomenon with a low degree of specifity, whose forces are the same as those responsible for the condensation of vapours and the deviations from ideal gas behaviour. The molecule of fluid keeps its identity along the adsorption-desorption process. It is always exothermic and the low interactions involved are of Van der Waals type. At high pressures, it generally occurs as a multilayer (molecules of adsorbate superposed and are not in contact with adsorbent) and achieves equilibrium fairly rapidly.

Nitrogen physisorption has extensively been used, since its weak interaction with the adsorbent is suitable for physisorption phenomenon. Adsorption isotherms are the relation between the amount adsorbed and the equilibrium pressure at constant temperature. When adsorption and desorption curves are not coincident, hysteresis occurs. It appears in the multilayer range of physisorption isotherms and it is generally associated with capillary condensation. These curves may have a wide variety of forms. Nevertheless, the majority may conveniently be grouped into six classes in the IUPAC classification [9-11].   The introduction of a number of simplifying assumptions, Brunauer, Emmett and Teller were able to extend the Langmuir mechanism [12-13], which is a theory for monolayer molecular adsorption, to multilayer adsorption [14]. The hypotheses of this theory are basically: (a) gas molecules physically adsorb on a solid in layers infinitely, (b) in the second and all higher layers, the energy of adsorption has the same value as the liquefaction energy of the liquid adsorbate, (c) there is no interaction between each adsorption layer and (d) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by (1):

$$\frac{p}{n(p^o - p)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \times \frac{p}{p^o} \tag{1}$$

where n is the specific amount of gas adsorbed at the equilibrium pressure p, n_m is the monolayer capacity and p_o is the saturation pressure. C is a constant, which is often assumed to be exponentially related to the adsorption energy. Thus, the BET plot should be a straight line with slope of $(C-1)/n_m C$ and intercept of $1/n_m C$. Then, the specific surface area, a(BET), can obtained from the BET monolayer capacity, n_m, by applying the following simple relation (2):

$$a(BET) = n_m L\sigma \tag{2}$$

where L is the Avogrado constant and σ is the average area occupied by each molecule in the complete monolayer.

Although BET method has become an extremely popular method for determining the surface area of adsorbents over the past 60 years, it presents important limitations and is applicable in a restricted p/p^o range (typically between 0.05 and 0.3). Therefore, other procedures (e.g. the α_S-method) should be used, when there is significant primary micropore filling contribution and when the structure of the completed monolayer varies from one surface to another [4, 15, 16].

Experimental Conditions

N_2 adsorption and desorption isotherms at 77 K were measured on a Micromeritics ASAP 2000 surface analyzer. Before analysis, the samples were degassed in vacuum and at higher temperature. The used gases were N_2 (Carburos metálicos, 99.999%) and He (Carburos metálicos, 99.999%). The surface area was calculated according to the BET method and the pore size distribution was determined by using the Barrett-Joyner-Halenda (BJH) method [17].

For microporosity analysis, N_2 adsorption and desorption isotherms at 77 K were measured on an automatic Micromeritics ASAP 2020 surface analyzer. Before analysis, the samples were degassed in vacuum at 120 °C for 16 h. The surface area was calculated according to the BET and DFT methods and the micropore size distribution was determined using the Micromeritics DFT software.

2.2.6   Chemisorption of hydrogen

An important application of chemisorption in catalysis is the determination of metallic area of a supported catalyst.

The chemisorption is the adsorption involving chemical bonding. It depends on the reactivity of the adsorbent and adsorptive. Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer. Since chemisorbed molecules undergo reaction or dissociation, they loose identity and cannot be recovered by desorption.

The gas employed as adsorbate should rapidly form the monolayer and its metal-adsorbate interaction stoichiometry should be considered. The adsorption conditions have to ensure that chemisorption is the predominant process.

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Considering the former statements, H$_2$ and CO are the most used gases for the determination of metallic area [15, 16].

Experimental Conditions

Hydrogen chemisorption was conducted in a Micromeritics ASAP 2010 apparatus. The used gases were H$_2$ (99,999%) and He (Carburos metálicos, 99.999%). The catalysts had been reduced *ex-sit*. Prior to the measurement, the samples were evacuated at 127 °C for 1 h, treated in flow of pure hydrogen (30 cm^3 min^{-1}) at 327 °C for 1 h, evacuated at 327 °C for 2 h, and finally cooled down to 37 °C for chemisorption. The amount of irreversibly adsorbed H$_2$ was measured using the double isotherm method [18]. From the first isotherm, measured in the 0-68 kPa pressure range, the total volume of hydrogen adsorbed was obtained. Then, the catalyst was evacuated (about 10–6 Torr) again at the chemisorption temperature for 10 min for back sorption measurements in order to obtain the volume of hydrogen reversibly adsorbed. The linear portion of each isotherm was extrapolated to zero pressure in order to estimate the total adsorbed volume and the reversibly adsorbed volume of hydrogen. The difference between two hydrogen uptakes provides the volume of irreversibly adsorbed hydrogen. The fraction of exposed palladium was calculated by the ratio of the irreversible uptake to the total metal content assuming an adsorption stoichiometry of 1:1.

2.2.7   Elemental Analysis

A combustion train is used to determine the elemental composition of a material. The analytical analyses of eluted gases from known amount of sample give the elemental composition (H, C, N, S).

Experimental Conditions

The elemental analyser used was a Carlo Erba EA1108 analyser.

2.2.8   Temperature-Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) studies the behaviour of a material in a reductive atmosphere, generally created by H$_2$, either in a temperature range or at a given temperature. If oxidative gases are used instead of H$_2$, the oxidability of the material may be studied (TPO). It is also possible to study desorption phenomena (TPD).
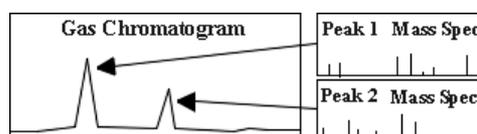
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The specimen is set in a furnace under a reductive gaseous stream. The eluted gases are analysed by TCD and/or a gas mass spectrometer. The signal is recorded by a computer and plotted versus time or temperature.

Experimental Conditions

The equipment for TPR/TPD/TPO experiments was a TPDRO 1100 ThermoFinnigan provided with a TCD detector and connected to a mass spectrometer QMS 422 Omnistar. The reductive gaseous stream consisted on a mixture of H_2 (5%) in Argon (Carburos Metálicos). Helium (Carburos Metálicos) was used in desorption analysis and O_2 (5%) in Helium (Carburos Metálicos) in the oxidation measurements. The temperature range was differently set in every study.

2.2.9   Gas chromatography – Mass spectrometry

Mass spectrometry is widely used in the powerful method of coupling Gas Chromatography (GC) with Mass Spectrometry (MS). Gas chromatography

separates compounds, which will be detected by the mass spectrometer.

A molecule (M), previously separated by the column in the chromatograph, enters the spectrometer (Fig. 2.2.5). It can be ionized by removal or addition of an electron (electron impact) to give species (M+ · and M- ; respectively) having a mass which, for practical purposes, is identical to that of the original molecule, the spectrometer known as ionizer [19].

In the ion *analyzer* region, those ions are analyzed to provide information about the molecular weight of the compound and its chemical structure. There are many types of mass spectrometers and sample introduction techniques which allow a wide range of analyses. The final element of the mass spectrometer is the *detector*. The detector records the charge induced or current produced when a mass passes by or hits a surface. In a scanning instrument the signal produced in the detector during the course of the scan versus *m/z* will produce a mass spectrum, a record of how many ions of each *m/z* are present.
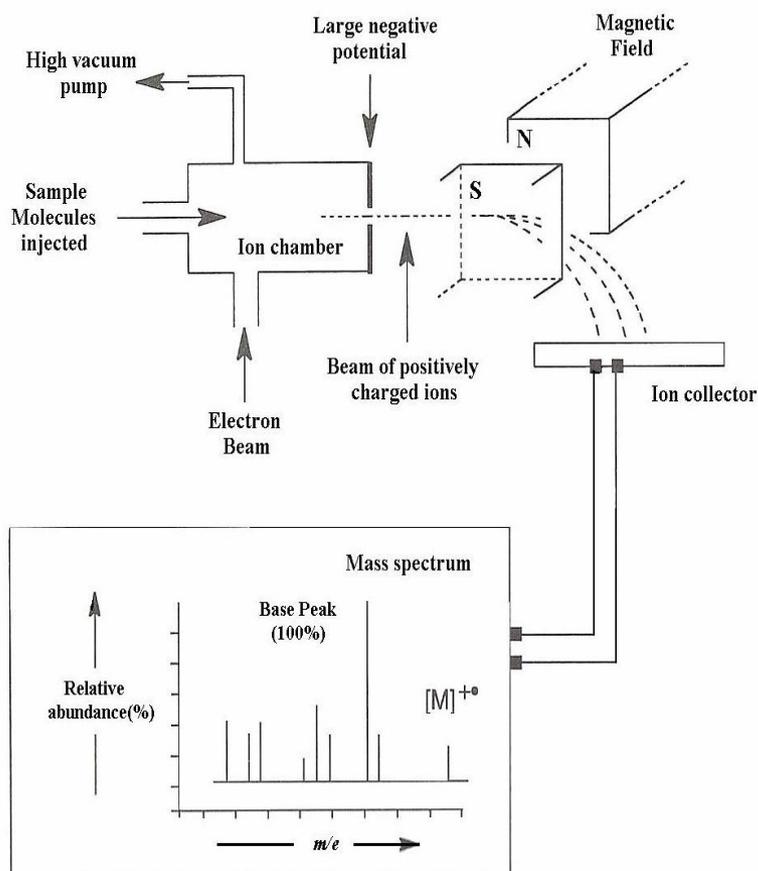
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Figure 2.2.5 Schematic diagram of an electron-impact mass spectrometer.

Experimental Conditions

An Agilent 6890 gas chromatograph coupled to a mass spectrometer with an isotopic relation Delta Plus Finnigan MAT and GC Combustion III Finnigan MATT interface was used. The same method as in gas chromatography analyse was applied (see *Chapter 2.1*).

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2.2.10 Ultraviolet spectroscopy (UV)

UV spectroscopy usually refers to electronic transitions occurring when a molecule is exposed to a radiation, whose wavelength (λ) is in the range 200-380 nm of the electromagnetic spectrum [20, 21].

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

1. Transitions involving π, σ, and n electrons
2. Transitions involving charge-transfer electrons
3. Transitions involving d and f electrons

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level [22]. Any spectral feature is due not to the whole molecule, but to an identifiable part of
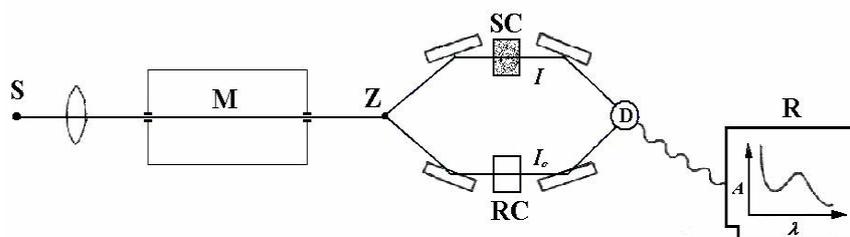

Figure 2.2.6 Schematic representation of a double beam spectrometer. **S**: source of radiation, **M**: monochromator, **Z**: beam separator, **SC**: sample cell, **RC**: reference cell (pure solvent or matrix), **D**: detector and **R**: register (computer, printer, screen) of absorption or transmission.

the molecule, which is called *chromophore*. The radiant energy is measured by a photoelectric device in practically all UV spectrophotometers. There are four basic components in such spectrophotometers: a source of radiant energy (Fig. 2.2.6): (a), the spectrometer or monochromator (b), the absorption-cell assembly (usually made of quartz) (c) and the photometer or detecting device (d). A deuterium lamp

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is used to obtain the radiation in the UV spectroscopic range. Normally double-beam instruments are used where the absorption of a reference cell, containing the solvent (ethanol, hexane, water or dioxan are usual solvents) or the matrix, is substracted from the absorption of the sample cell [19, 21]. The reference cell contained a mixture of ethyl linoleate, oleate and stearate in ethanol (solvent).

By applying the Beer-Lambert Law (absorptivity is proportional to concentration and path length), quantitative analyses are possible. In our case, UV spectroscopy was used as a qualitative technique in order to determine the structure of the *unknown* compounds.

Experimental Conditions

The reference simple consisted in a mixture of ethyl oleate, linoleate and stearate in ethanol. The UV-visible spectra were recorded in a spectrophotometer Dinko 8500 using a wolfram and deuterium lamp for the visible and UV region, respectively.

2.2.11 Proton Nuclear Magnetic Resonance (^{1}H-NMR)

All nuclei possess charge because they contain protons and some of them also behave as if they spin. NMR spectroscopy is related to the movement of nuclear spin. A magnetic field **H** is associated to the spinning charge, since it is equivalent to a conductor carrying a current. Such nuclear magnetic dipoles are characterized by nuclear magnetic spin quantum numbers designated by the letter **I**, which can take values equal to 0, $^1/_2$, 1, $^3/_2$…etc. These nuclei possess only certain permitted orientations ($2\mathbf{I}+1$) under the influence of a uniform magnetic field. The two most important studied nuclei are ^{1}H and ^{13}C, which both have $\mathbf{I} = {}^1/_2$; therefore, the nuclear spin can only have two values related to the quantum numbers, $+^1/_2$ (α) and $-^1/_2$ (β). When these nuclei are situated under the influence of a uniform magnetic field, they tend to align with the field or opposite the field. These two orientations will be of unequal energy, so it is possible to induce a spectroscopic transition (spin-flip) by the absorption of a quantum of electromagnetic energy of an appropriate frequency (ν). In this case, the required energy also depends on the strength of the applied field, $\boldsymbol{H_o}$. The Larmor equation gives the value of ν depending on the applied magnetic field:

$$\nu = K\,\boldsymbol{H_o}$$

where K is a constant characteristic of the nucleus observed. The energy differences are then proportional to the magnetic field and extremely small value of energy. Since a magnetic field is always necessary to observe NMR phenomenon, a magnet becomes an essential part in any NMR spectrometer (Fig. 2.2.7) [19]. All magnets used share the following features: a) the magnetic field (B_o) must be strong, due to the fact that the sensitivity increases with the strength of the magnet, b) the magnetic field must be homogeneous to avoid distortion and broadening of the bands and, finally, c) the magnetic field must be stable. The sample is set between the two poles in a tube rotating as the arrow shows. The excitation of nuclei is achieved by a high frequencies transmitter. A current to the receiver is induced by the magnetization because of spin inversion. This signal is registered, amplified and plotted to give place to the spectrum

There are two kinds of NMR spectroscopy: pulsed Fourier transform (PFT), where all nuclei are excited simultaneously, or continuous wave (CW) NMR spectroscopy, where a seep or scan through a range of frequencies is performed.

NMR spectroscopy could be used so far to detect certain nuclei and to estimate them quantitatively. However, the real usefulness is based on secondary phenomena, the chemical shift (the frequency difference between the resonance of a
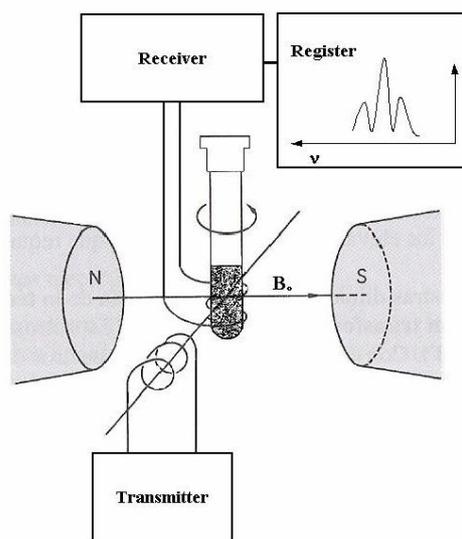

Figure 2.2.7 Schematic representation of a NMR spectrometer.

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nucleus and the resonance of reference compound) and spin-spin coupling (when one nucleus can sense the presence of other nuclei through the bonds of the molecule, the signal will split or multiple), which both reflect the chemical environment of the nuclear spins.

A ^{1}H NMR spectrum represents the resonance frequency (chemical shift, given in ppm to have the same scale irrespectively of the strength of the magnetic field) vs. the intensity of resonance frequency absorption by the sample [8, 19, 21]

Experimental Conditions

The simples were previously diluted in deutered chloroform. The analyses were performed in a Varian Gemini 300 and a Varian Mercury Vx 400 MHz.

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