Chapter 2

Experimental

2.0 EXPERIMENTAL PROCEDURE

2.1 Catalyst Precursors

All solids were obtained by precipitation. Small scale preparation (200 ml – 400 ml) to scan the parameter range was carried out in a Mettler-Toledo DL 77 Titrator to which an automated Rondo sample changer was attached (Figure 2.1). The Rondo was modified in such a way that the samples could be immersed in a water bath for a range of temperature. As starting material AHM (Ammonium Heptamolybdate), Na_2MoO_4 (Sodium Molybdate), Li_2MoO_4 (Lithium Molybdate), K_2MoO_4 (Potassium Molybdate) dissolved in water at a concentration range between 0.28 and 2 M were used. HNO_3 (1 M – 5 M) was used as precipitation agent. The precipitation experiments were carried out at 30 °C, 50 °C and 70° C. The solution was stirred at the rate of 2 ml/min. The white precipitate was filtered without any washing treatment and finally dried in a desiccators consist of silica gel under vacuum. The detail of the synthesis work is done by Abdullah. [61]. The list of samples prepared is shown in Table 2.1 below.

Fig. 2.1 Setup of Mettler-Toledo DL 77 Titrator.

Table 2.1 List of Precursors prepared by precipitation method.

No.	Cation	Sample No.	[Mo] / M	[HNO$_3$] / M	T / °C
1	K^+	249	0.28	2	30
2		219	0.28	2	50
3		229	0.28	2	70
4		250	2	2	30
5		245	2	2	50
6		244	2	2	70
7		253	2	5	30
8		246	2	5	50
9		243	2	5	70
10		254	0.28	5	30
11		247	0.28	5	50
12		233	0.28	5	70
13	Li^+	251	0.28	2	30
14		222	0.28	2	50
15		230	0.28	2	70
16	Na^+	252	2	2	30
17		226	2	2	50
18		231	2	2	70
19		255	2	5	30
20	NH_4^+	256	0.7	1	30
21		227	0.7	1	50
22		232	0.7	1	70
23		257	1	1	30
24		228	1	1	50
25		258	1	5	30
26		248	1	5	50
27		225	1	2	50
28		223	0.7	2	50

2.2 Theory on Analytical Methods Used

2.2.1 Powder X-ray Diffraction (XRD)

In November 1895, Wilhelm Röntgen discovered X-rays. He found that unknown rays (X-ray) were being emitted form the walls of a glass tube while the cathode rays tube was running. From this, he has developed the diagnostic method for medical and industrial users. Max von Laue in 1912 has developed the field of X-ray crystallography of which X-ray powder diffractometry is one important member. Von Laue has proved that X-rays can be diffracted by a crystal. W.L.Bragg in 1912, began investigating von Laue's X-ray patterns. He observed that X-ray reflects from a plane of atoms inside the crystal. The penetrating X-rays which travel into the internal layer, is reflected and travels back over the same distance before being reflected back to the surface. The distance traveled depends on the separation of the layer and the angle at which the X-ray entered the material. For this wave to be in phase with the wave which is reflected from the surface, it needs to have traveled a whole number of wavelengths while inside the material.

Powder XRD (X-ray Diffraction) is perhaps the most widely used X-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of crystalline material to be studied. The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d-spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the phase of the material.

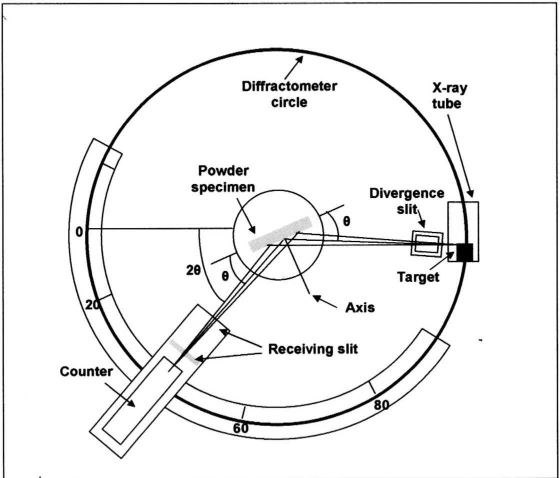

Fig 2.2 Schematic of X-ray Diffractometer

For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure.

In X-ray diffractometry, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament. A high voltage, typically 15-60 kV, is applied within the tube. The high voltage accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. The wavelength of these X-rays is characteristic of that target. These X-rays are collimated and directed onto the sample which has been ground to a fine powder (typically to produce particle sizes of less than 10 microns). A detector detects the X-ray signal; the signal is then processed electronically, converting the signal to a count rate. Changing the angle between the X-ray source, the sample and the detector at a controlled rate between preset limits is an X-ray scan (Figure 2.2).

The production of X-rays

X-rays are produced when fast-moving electrons impinge on matter. The phenomena resulting from the deceleration of such electrons are very complex, and X-rays result from two general types of interaction of the electrons with the atom of the target material. A high-speed electron may strike and displace a tightly bound electron deep in the atom near the nucleus, thereby ionizing the atom. When a certain inner shell of an atom has been ionized in this manner, an electron from an outer shell may fall into the vacant place, with the resulting emission of an X-ray characteristic of the atom involved.

X-ray Tube

X-rays are produced by streaming electron across an extremely high voltage potential (15-45 kV). The voltage is applied to a filament (typically a tungsten cathode) in a vacuum. The electrons are then accelerated into a metal target (typically cobalt and copper anode). The energy released results in two types of X-radiation. The first type is known as white radiation and consists of a broad, continuous spectrum containing many wavelengths of radiation. It is a result of the very rapid deceleration of electrons as they encounter the strong fields of target metal. As the electrons collide, they lose energy and that energy goes into making X-ray photons. The second type is called characteristic radiation. This radiation represents wavelengths that depend only on the structure of the target atoms. This is why characteristic X-rays can be utilized to reveal the structural information of a material. In the X-ray diffractometer, the tube provides an X-ray source. This is why X-ray tube is one of the important part in X-ray diffractometer or we called it, the heart of an X-ray diffractometer (Figure 2.3).

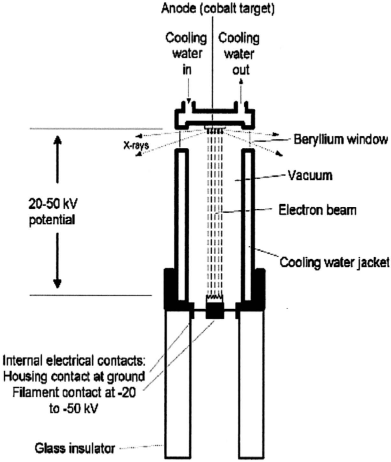

Fig.2.3 Schematic of X-ray Diffraction tube [1].

Detectors

There are varieties of detectors used in XRD systems. The most common detectors used for powder X-ray diffractometer are scintillation counter and position sensitive detector (PSD). All X-ray detectors, however, have one thing in common, in that they all depend upon the ability of X-rays to ionize matter.

In the scintillation detector, the conversion of the X-ray photon energies into voltage pulses is a two stage process. In the first stage, the X-ray photon is converted into flashes of blue light by means of a phosphor, or scintillator, which is a substance that has the property to absorb radiation at a certain wavelength, then re-emit radiation at a longer wavelength. For work in the X-ray region it is common to use phosphors of sodium iodide doped with thallium. These phosphors emit light photons with wavelengths of around 4100 Å. In the second stage of the process, the blue light from the phosphor is converted to voltage pulses by means of a photomultiplier. Here the light photons fall onto an antimony/cesium photocathode, each producing a burst of electrons which are then focused onto a chain of typically ten further photosurfaces called dynodes. Each of these dynodes has a successively higher potential and the electrons produced at each dynode are accelerated to the next, such that at the following dynode more electrons can be produced by means of the kinetic energy gained by acceleration. This total effect gives an increase or gain in the signal. After the last dynode, the electrons are collected by the anode and a voltage pulse is formed in a similar way to that already described for the gas counter (Figure 2.4).

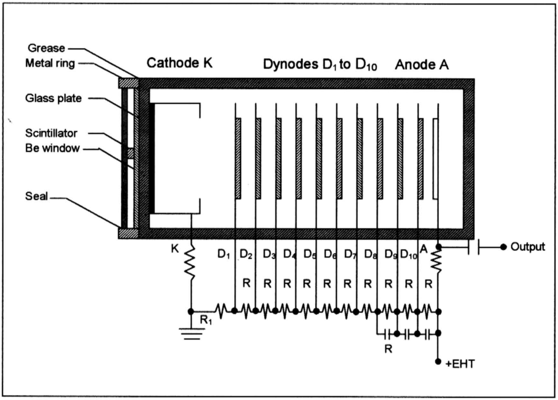

Fig. 2.4 Scintillation counter

Position-sensitive detectors (PSD) is essentially a gas proportional detector in which electron collection and pulse-generating electronics are attached to both ends of the anode wire. PSD are finding increasing application in X-ray powder diffraction, mainly because of the advantage they offer in increased speed of data acquisition. In its simplest configuration, the PSD is essentially a gas proportional detector in which electron collection and pulse generating electronics are attached to both ends of the anode wire. The anode wire is made to be poorly conducting to slow down the passage of electrons. By measuring the rate at which a pulse develops at each end of the wire, it is possible to correlate the rise times with the position along the anode wire where the ionisation originated. Since the PSD is able to record data from a range of angles at one time, it offers special advantages to those cases where speed of data acquisition is critical. The development of the electronics required to permit a PSD to continuously scan two θ ranges beyond its aperture have decreased powder pattern collection times to a few seconds. The effective angular resolution of the PSD is equivalent to a few hundredths of a degree 2 θ, although this resolution is somewhat worse than can be obtained using a classical diffractometer, it is more than sufficient for most applications (Figure 2.5).

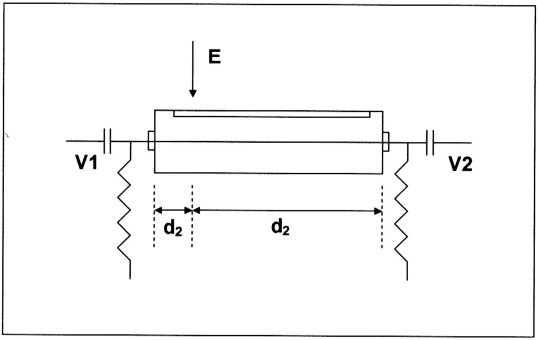

Fig 2.5 The position-sensitive detector: E=incoming X-ray photon; V1 and V2=voltage at capacitors 1 and 2 respectively, d1 and d2=distances from the entry point of the photon to sides 1 and 2 of the detector, respectively.

Monochromator

X-rays are produced in three main wavelengths, $K_{\alpha 1}$ and $K_{\alpha 2}$ from white radiation which have similar wavelengths and K_{β} which has a shorter wavelength and so higher energy (Figure 2.6). Since having K_{α} and K_{β}, X-rays will double the number of diffraction peaks and so confuse the pattern, K_{β} X-rays are therefore removed with a filter or monochromator. When source electrons strike these inner shell/orbital electrons, the electrons get bounced out of position (in other words the electrons undergo an energy transition). This event is immediately followed by another electron dropping back toward the nucleus. The loss in energy appears as an emitted photon with a characteristic frequency. The amount of energy released will depend upon the number of protons and neutrons in the nucleus and the shell from which the electron was displaced. The diffracted beam monochromator consists of a single crystal mounted behind the receiving slit with a detector set at the correct angle to collect the wavelength of interest diffracted by the monochromator. A monochromator can be placed between the source and the specimen (incident beam), or between the specimen and the detector (diffracted beam). The actual band pass value for a given monochromator will depend upon the widths and positions of limiting apertures which are placed somewhere on the focusing circle of the monochromator.

The more common instrumental methods of monochromatization include:

- Use of a β-filter
- Use of a proportional detector and pulse height selection
- Use of a Si(Li) solid state detector
- Use of a diffracted-beam monochromator
- Use of a primary beam monochromator.

The basic purpose of the monochromatization of the diffracted radiation is to obtain an experimental pattern from a single wavelength. Inspection of the Bragg law reveals that each unique d-spacing will diffract different wavelengths at their own unique diffraction angles. Thus, if a pattern were measured using an X-ray beam containing two wavelengths, the observed pattern would, in fact, be two patterns (one for each wavelengths) superimposed, one on top of the other, and clearly will be more difficult to interpret than a diffractogram from two known wavelengths. Much more of a problem occurs when additional unknown wavelengths are diffracted.

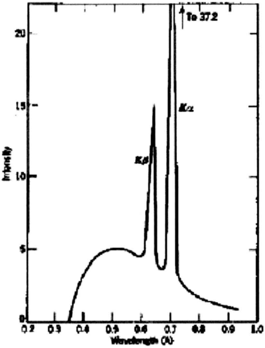

Fig. 2.6 Characteristic lines of copper superimposed on the white radiation spectrum

Bragg's Law

When an X-ray beam hits a sample and is diffracted, the distances between the plane of the atoms could be determined by applying Bragg's Law.

For constructive interference to occur, the emerging beams A′, B′, C′, D′, as shown in Figure 2.7 regenerate a plane wavefront corresponding to the incident wavefront ABCD. The ray BB′ that strikes the second plane travels further than the ray AA′, and the ray CC′ goes further still. The extra distance traveled by BB′ relative to AA′ is 2d sin θ, where d is the interplanar distance and θ is the angle of incidence [28]. Bragg expressed this in an equation now known as Bragg's law:

$$2d \sin \theta = n\lambda \qquad [2.1]$$

where;

θ is the angle between the incident rays and the surface of the crystal

d is the spacing between two layers of atoms

λ is the wavelength of the rays

n is an integer.

The integer *n* reflects the number of 'extra' wavelengths traveled by BB′, or the number of cycles that BB′ is retarded relative to AA′ and *n* is called the order of the reflection. Reflection with n=2, 3,… are called second order, third order, and so on. It follows that a bright reflection should be observed when the glancing angle satisfies the Bragg's Law.

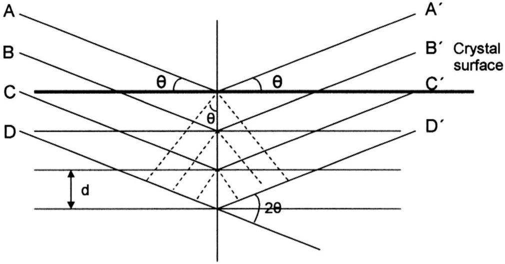

Fig.2.7 Bragg reflection of X-rays from parallel planes of atoms

The preparation of samples is one of the critical steps in many analytical methods and particularly for X-ray powder diffraction (XRD) analysis. Depending on the nature of the powder XRD study and the desired results, sample preparation can be of minimal importance or it can be crucial. If a qualitative analysis of a simple, familiar material is desired, the material can be quickly ground in a mortar and packed into a cavity type sample holder, paying no attention to orientation or particle size effects. On the other hand analyses of complex materials involving search/match procedures, quantitative phase analysis, lattice parameter refinement, or Rietveld refinement of crystal structures require much more careful attention to the method and execution of sample preparation and mounting. The two most important results desired in these more complex cases are accurate and precise line positions and intensities.

The effect of grinding the material is to broaden some or all reflections and to produce small amounts of amorphous surface layers. Materials will usually begin to show some particle size related broadening when individual crystallites are smaller than about 1000 Å. It is important to realise, however that the position of a broadened reflection may be shifted from the position of the unbroadened reflection. Overgrinding can induce phase transformation and solid state reactions. Accurate data on peak position will be obtained from a thin sample. For this reason, sample amounts of a few layers of powder on a double-stick film in a well-aligned diffractometer will yield accurate peak positions. A thick sample with a random orientation of crystallites will produce less accurate peak positions because of absorption/displacement effects but can produce good intensity data.

Most samples to be examined by powder diffraction methods require mounting of the (powdered) sample in an appropriate holder, and this step can give rise to systematic errors affecting both reflection positions and intensities. Although sample mounting errors are not always obvious, they generally produce the most common errors in peak position and intensity encountered in X-ray powder diffraction analysis. Attention to sample packing is important because diffraction occurs from a volume of sample, not just the surface. Loose sample packing can give rise to transparency effects in addition to those related intrinsically to the sample. Systematic errors related to sample packing and thickness are relatively unimportant for materials having high linear absorption coefficients, since the incident X-ray beam penetrates little more than a single layer of crystallites on the surface of the samples.

Ideally the surface of a mount should be flat, with no roughness or curvature, and not tilted in any direction. Any roughness or curvature has the potential to produce systematic deviations in the positions and breadths of observed reflections related to sample height displacement and flat specimen error. There are two common types of sample holder, reflection and transmission. Transmission sample holder need a very small amount of sample and the preparation is easy and clean (Figure 2.8). Variables of sample displacement can be corrected by a micrometer screw. The reflection technique needs to be applied in all cases where transmission and capillary technique cannot be used for example the measurement of bulky material, liquids and thin layer (Figure 2.9). Position of samples in a stable height can be adjusted using a reference blade.

Problem that can occur in sample preparation is called preferred orientation which usually occurs with rod or plate-like particles. For example, plate-like particles tend to lie flat on the sample holder; very few will have a perpendicular orientation. As there is no longer a random orientation of crystallites, some of the X-ray reflections that could be expected are unusually weak or missing altogether. For powder samples, the samples are further grind to reasonably fine particles to minimize preferred orientation. Considerable effort must be expended in sample preparation to achieve the random state, and it is often difficult to determine when randomness is attained unless one has a reference set of intensities that are known to represent the random sample.

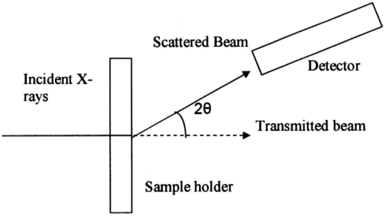

Fig 2.8 Schematic of transmission sample holder

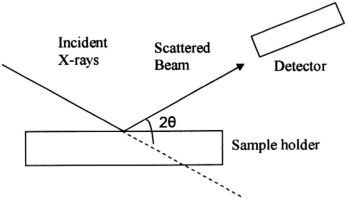

Fig 2.9 Schematic of reflection sample holder

Amorphous and Crystalline Material

In X-ray powder diffractometry one is generally dealing exclusively with crystalline (ordered) materials because it is only sensitive to crystalline phase. The diffraction pattern can be used to determine the degree of crystallinity. The most dramatic difference among crystalline and amorphous materials is in how they scatter an X-ray beam. The crystalline forms produce sharps line due to diffraction, whereas the amorphous usually produces a broad peak indicating only some short range order in the atomic arrangement. The atomic arrangement is not recurring in three dimensions and do not give Bragg reflections. This does not mean that their atomic structure is totally disordered because the disorder of the matter is perfect only in the case of diluted monoatomic or inert gases. In fact the so-called amorphous solids always exhibit a short-range order, for instance in silica gel. Small particles with sizes below 1.0-1.5 nm constitute a particular category of solids which have no long-range order in that the interatomic distances are at most equal to the diameter of the particles.

Some materials are X-ray amorphous investigate by XRD but shows crystalline structure in TEM, this could be due to crystallite size which XRD could not detect particle size less than 30-40 Å. Much of the solid matter we meet in our daily contacts shows little outward evidence of crystallinity. The X-ray beam is reflected by a specific set of lattice planes in the powder because of the random orientation of the microcrystals in the powder, all possible lattice planes will reflect sooner or later. The term, amorphous solid is reserved for those few substances that show no crystalline nature. Glasses and polymers fall in this class [29].

Interpretation of Powder X-ray Diffraction

In early diffraction experiments, computers were used for data interpretation only. Elaborate experiments were cumbersome, time consuming, and required direct supervision by the operator. Today the computer also runs the experiment, and it also can process and interpret the data without any input from the operator. Every crystalline material gives a unique X-ray diffraction pattern. Study of diffraction patterns from unknown phases offers a powerful means of qualitative identification. The problem is one of pattern recognition between the unknown and a database of single phase reference patterns. Although the potential for qualitative phase identification was certainly recognised from the very early days of X-ray diffraction, the first attempts to list standard diffraction patterns were not published in detail until the mid-1930's. Phase identification is accomplished by comparing the data (peaks and relative intensities from a very large set of data provided by the International Center for Diffraction Data (ICDD) (formerly ASTM then JCPDS).

It is a collection of single phase X-ray powder patterns in the form of tables of characteristic interplanar spacings and corresponding relative intensities along with crystallographic properties. The file is available in printed form and as computer-readable media (tape and CD-ROM). It is sometimes difficult to identify specimens such as catalysts. They are composed of a mixture of several phases which can be poorly crystalline or in a state of fine division.

There are three types of information in a diffraction pattern; the position, the intensity, and the shape of the diffraction peaks. The positions of the diffraction peaks are determined by the geometry of the crystal lattice, *i.e.*, the size and shape of the unit cell. The intensities of the peaks in a pattern are related to the specific atoms in a crystal and their arrangement in the unit cell of the crystal structure. The diffraction profile is related to the size and perfection of the crystallites under study and to various instrumental parameters. The peak positions are fairly easy to determine accurately by diffraction methods; whereas the intensities and the profiles are considerably more difficult to measure accurately. Consequently, most analytical methods emphasize the position variables (the d-spacing) and rely less on the other two parameters unless the intensities (*e.g.*, quantitative analysis or structure refinement) or the profile parameters (*e.g.*, crystallite size and strain) are specifically required.

Different polymorphs have different crystal structures due to a different packing of the molecules in the lattice. This results in a different crystal symmetry or unit cell parameters which directly influence the reflection characteristics of powders.

A different polymorph will in general diffract at a different set of angles and will give other values for the intensities. Therefore X-ray powder diffraction can be used to identify different polymorphs or a mixture of polymorphs in a reproducible and reliable way [30]. Experimental setup requires that, if a reflection is diffracted when the incoming beam forms an angle θ with a certain lattice plane, the reflected beam is recorded an angle 2 θ.

Although 2 θ values are part of the printed output, normally peaks are characterized by their unique d-value. The combination of the unique set of angles at which a powder reflects X-rays and the corresponding intensities, yields a fingerprint that is unique for the crystal structure. The hump (absence of peaks) in the data implies the presence of amorphous or very poorly crystalline phases. In theory, pure amorphous material would give no hump at all and would not reveal its presence easily by XRD, except perhaps by helping to raise the background level [31]. Peaks shifts can occur for several reasons, real and artificial peak shift. Real peak shift may due to different temperature apply on the same sample during the XRD measurement, same temperature but with different type of doping, or could be due to difference in lattice parameter in the same sample. Artificial peak shift may due to poorly aligned of diffractometer results geometry displacement, displacement of sample holder, poor or sloppy sample packing and the phase could be substituted or 2 θ offset whereby sample is in current position except 2 θ scale is shifted [32]. The process of assigning *hkl* values to the diffraction lines in the pattern of a new phase is known as indexing a pattern. In recent years, computer procedures have been developed for solving this problem in symmetries as low as triclinic. During the process of indexing, several possible solutions may result from trial unit cells

2.2.2 Raman Spectroscopy

Raman Spectroscopy is an analytical method based on measurements of radiation scattered from a given sample. The method is named after the Indian physicist Chandrasekhara V. Raman (1888-1970), which was the first to observe the effect experimentally (in 1928) (C. V. Raman and K. S. Krishnan, "A new type of secondary radiation", Nature 121, 501 (1928)) [33]. Due to the fact that it could provide valuable information on the structure of samples at the molecular level, it received considerable attention as a method of non-destructive chemical analysis in the years following its initial discovery.

Raman spectroscopy is based on the detection of light which interacts with a substance. It can do so in three main ways; the light may be absorbed, it may be transmitted through the sample unchanged or it may be scattered. Figure 2.10 illustrates the general principle of the measurement, which is that the light from a powerful monochromatic light source (a laser) is focused onto the sample of interest and as many as possible of the photons that scatter from the sample are collected and dispersed in a spectrometer. The photons that are scattered elastically comprise the Rayleigh scattering, which is intense but carries no vibrational information and so is filtered out of the signal. In addition to the Rayleigh scattering, Raman scattering, in which the frequency of the incident photons changes due to interaction with the sample, can also be detected [34].

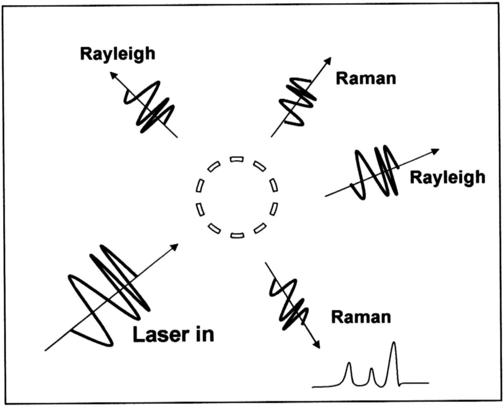

Fig. 2.10 The general principle of measurement, Raman effect.

A strong point of Raman spectroscopy for research in catalysis is that the technique is highly suitable for *in situ* studies. The spectra of adsorbed species interfere weakly with signals from the gas phase, enabling studies under reaction conditions to be performed. A second advantage is that typical supports such as silica and alumina are weak Raman scatterers, with the consequence that adsorbed species can be measured at frequencies as low as 50 cm^{-1}. This makes Raman spectroscopy a powerful tool to study catalytically active phases on a support [36].

Vibrational Structure via Raman and Infrared Spectroscopy

Infrared spectroscopy is an absorption technique, where the molecule absorbs radiation of frequencies of the molecule. Not all vibrations may be active in the infrared, however, Raman spectroscopy is a complimentary technique to IR which makes use of scattering of radiation instead of absorption. Vibrations which are not active in the IR may be active in the Raman so using both techniques often gives much more information than just using one alone. A general selection rule for the absorption of a photon is that the dipole moment of the molecule must change during the vibration. This distinguishes infrared from Raman spectroscopy, where the selection rule requires that the molecular polarisability change during the vibration.

The number of different vibrations that a molecule possesses follows from the following considerations. A molecule consisting of N atoms has 3 N degrees of freedom. Three of these are translational degrees of freedom of the molecule and three are rotations of the molecule along the three principle axes of inertia. Linear molecules have only two rotational degrees of freedom, as no energy is involved in the rotation along the main axis. Thus, the number of fundamental vibrations is 3 N-6 for a non-linear and 3 N-5 for a linear molecule. In addition, there are overtones and combinations of fundamental vibrations. However, not all vibrations are visible. There are four types of vibration, as illustrated by Fig. 2.11, each with a characteristic symbol:

- Stretch vibrations (symbol υ), changing a length of a bond,
- Bending vibrations in one plane (symbol δ), changing bond angles but leaving bond lengths unaltered (in larger molecules further, twist and wag vibrations),
- Bending vibrations out of plane (symbol γ), in which one atom oscillates through a plane defined by at least three neighbouring atoms,
- Torsion vibrations (symbol τ) changing the angle between two planes through atoms.

Generally, the frequencies of these vibrations decrease in the order $\upsilon > \delta > \gamma > \tau$. In addition, vibrations are divided into symmetric and asymmetric vibrations (υ_s and υ_{as})

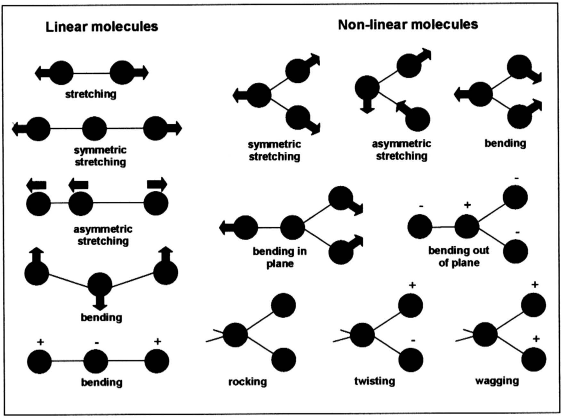

Fig. 2.11 Fundamental vibrations of several molecules.

Raman Instrumentation

Raman spectra are electromagnetic spectra in the optical range. Raman spectra are emission spectra excited by monochromatic radiation in the ultraviolet (UV, 0.2 ... 0.4 μm ≈ 5000 ... 25000 cm^{-1}), visible (VIS, 0.4 ... 0.7 μm ≈ 25000 ... 14300 cm^{-1}), or near infrared (NIR, 0.7 ... 2.5 μm ≈ 14300 ... 4000 cm^{-1}) region. They are due to modulation of incident light by molecular vibrations. A Raman spectrometer usually combines a radiation source, a sample arrangement, a device for spectral dispersion or selection of radiation, and a radiation detector, connected to appropriate recording and evaluation facilities (Figure 2.12). An ideal spectrometer records completely resolved spectra with a maximum signal to noise ratio.

A typical Raman spectrometer is made up of three basic parts; the laser, the collection device and the spectrograph. A laser is used to excite Raman spectra because it gives a coherent beam of monochromatic light. This gives sufficient intensity to produce a useful amount of Raman scattering. Lasers used for Raman spectroscopy must exhibit good wavelength stability and low background emission. A probe is used as a collection device that collects the scattered photons, filters out the Rayleigh scatter and any background signal from the fiber optics cables, and sends the Raman scatter to the spectrograph. Many probes also focus and deliver the incident laser beam. When Raman scattered photons enter the spectrograph, they pass to a detector, which records the intensity of the Raman signal at each wavelength. This data is plotted as the Raman spectrum.

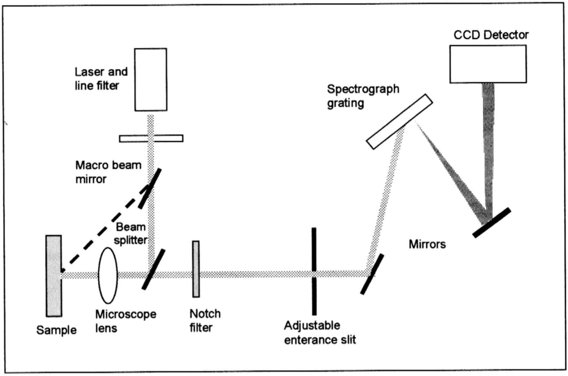

Fig 2.12 Schematic diagram of Raman spectrometer

Raman Scattering

A molecule is considered to be subjected to an electromagnetic field of radiation of frequency ν. This frequency is defined as the exciting radiation, and can be chosen in a range of frequencies, ν. The photons can be absorbed by the molecules if their energy $E = h\nu$ corresponds exactly to the difference between the ground state energy level and an excited one. This is the absorption process. After absorption the photons are re-emitted in all directions, without a change in frequency. This process is elastic scattering or the Rayleigh effect. However, in some cases, scattering occurs with a frequency shift corresponding to an elastic collision between the molecule and the photon. This is the Raman effect, which can give information on the vibrational energy levels of the molecule.

The Raman effect arises when the incident light excites molecules in the sample which subsequently scatter the light (as shown in Figure 2.10). While most of this scattered light is at the same wavelength as the incident light, some is scattered at a different wavelength. This inelastically scattered light is called Raman scatter. It results form the molecule changing its motions. The energy difference between the incident light (Ei) and the Raman scattered light (Es) is equal to the energy involved in charging the molecule's vibrational state (getting the molecule to vibrate, Ev). This energy difference is called the Raman shift.

$$Ev = Ei - Es$$

Raman scattering is a powerful light scattering technique used to diagnose the internal structure of molecules and crystals. In a light scattering experiment, light of a known frequency and polarization is scattered from a sample. Raman scattered light is frequency-shifted with respect to the excitation frequency. Several different Raman shifted signals will often be observed; each being associated with different vibrational or rotational motions of molecules in the sample. Raman scattering comprises a very small fraction of the incident photons, typically 0.0001 %, hence the need for an intense source and sensitive detector. The energy levels in a molecule that is undergoing Raman scattering can be represented by Figure 2.13. The molecules are in their ground electronic states before and after scattering.

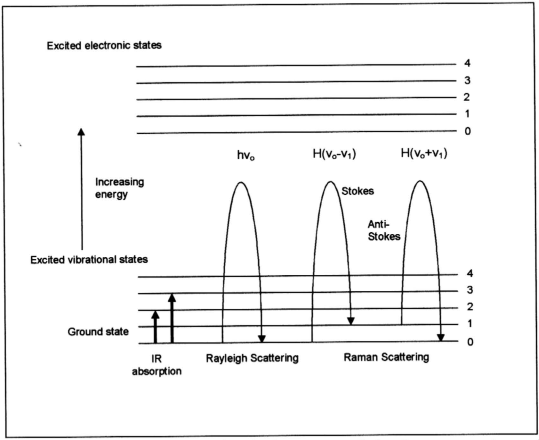

Fig 2.13 Energy level diagrams of Rayleigh scattering, Stokes Raman scattering, and anti-Stokes Raman scattering

In a very small number of scattering events, some incident light energy is absorbed by the molecule resulting in an increase in the bond vibration energy (second transition in the diagram). A net loss in the exciting photon energy occurs, equal to that absorbed by the bond and given by $h(v_o - v_1)$ where v_1 is the bond vibrational frequency. The light is effectively shifted by the process, called *Stokes* scattering.

Thermal energy absorbed by the molecule can raise the vibrational energy (ground state) of some molecules and if scattering of light occurs from these molecules, photons can exit with increased energy, $h(v_o + v_1)$. This is termed *anti-Stokes* scattering. The number of *anti-Stokes* scattering events is depending upon the thermal energy of the molecule (vibrational energy) and hence temperature. However, the *Stokes* scattering is temperature independent.

A molecule that scatters light elastically (Rayleigh scattering) is represented by the first transition (on the left). Light impinging on the molecule leaves with the same energy; there is no net change to the molecule or light energies. Photons leave the molecule with the same energy, hv_o. In Rayleigh scattering, the emitted photon has the same wavelength as the absorbing photon which is intense but carries no vibrational information and so is filtered out of the signal. .

Raman is a form of vibrational spectroscopy. This means that these energy transitions arise from molecular vibrations. Because these vibrations involve identifiable functional groups, when the energies of these transitions are plotted as a spectrum, they can be used to identify the molecule.

Polarisation

The polarisability dependent on how tightly the electrons are bound to the nuclei. In the symmetric stretch the strength of electron binding is different between the minimum and maximum internuclear distances. Therefore the polarisability changes during the vibration and this vibrational mode scatters Raman light (the vibration is Raman active). In the asymmetric stretch the electrons are more easily polarised in the bond that expands but are less easily polarized in the bond that compresses (Figure 2.14).

The Raman Spectrum

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation, (usually in units of wavenumbers, cm^{-1}). This difference is called the *Raman shift*. Note that, because it is a difference in value, the Raman shift is independent of the frequency of the incident radiation. Typically, only the Stokes region is used (the anti-Stokes spectrum is identical in pattern, but much less intense) (Figure 2.15).

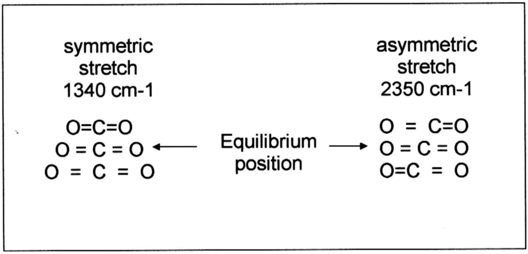

Fig 2.14 Examples of Raman active and inactive vibrations in CO_2

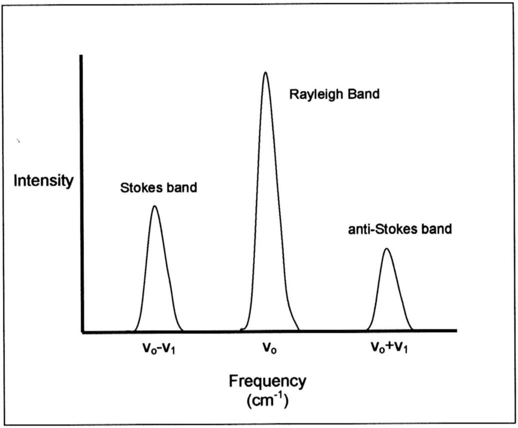

Fig 2.15 Raman spectrum

2.3 Experimental Work

2.3.1 X-ray Diffraction Experiment

XRD measurement in the thesis was made on a STOE STADI-P focusing monochromatic transmission diffractometer (Ge primary monochromator, Cu $K_{\alpha 1}$ radiation, theta-theta mode), equipped with a linear position sensitive detector (linear PSD) at room temperature. The scanning range was applied from 2 to 90 ° and the scan speed was done at 0.1 °/step. The phase analysis was done with the STOE Win XPOW software package (version 1.06, Stoe Darmstadt, Germany), PowderCell (V2.3) software package, FINDLT, and Diamond Softwares.

2.3.2 Raman Spectroscopy Experiment

Raman spectra were recorded with a DILOR LABRAM 1 spectrometer equipped with a confocal microscope (Olympus). The spectrometer is equipped with a CCD camera which is Peltier cooled to 243 K to reduce the thermal noise. Laterally varying sample structures can be identified on a micrometer scale by Raman imaging and related to inhomogeneous sample compositions. He-laser (632.8 nm) was used for the excitation of the Raman spectra. A notch filter was applied to cut off the laser line. Each spectrum shown is the addition of 5 accumulations each integrated for 60 seconds.

2.3.3 Transmission Electron Microscopy Experiment (TEM)

Transmission Electron Microscopy (TEM) analysis was performed on a CM 200 electron microscope (Philips) (point resolution: 0.2 nm, acceleration voltage: 200 kV) equipped with an EDX system. A small amount of oxide powder was crushed in corundum mortars to form finer powder if necessary. This specimen powder was dispersed in a neutral organic solvent (ethanol) by ultrasonic stimulation. A small droplet of such a suspension, typically several μl, was brought on a copper grid covered by a carbon microrgid.

2.3.4 Scanning Electron Microscopy (SEM) and Electron Diffraction X-ray (EDX) Experiment

The morphology and size of the particles was determined by Scanning Electron Microscopy (SEM) which was conducted with the Hitachi S-4000 microscope. The acceleration voltage was set at 5 kV and the working distance was 10mm.