CHAPTER 2

EXPERIMENTAL METHODOLOGY

Abstract

The preparation of catalysts is frequently described as an art, and a catalyst recipe may specify detailed and arcane procedures that appear to be necessary in order to achieve reproducibility and the desired products. The process chosen for the preparation of catalyst represents a balance between the cost of preparation and the degree to which the ideal chemical and physical properties are achieved. Most practical catalysts are highly complex materials, and a basic problem is how to correlate catalyst behaviour with physical and chemical structure. During the past decade several ingenious ways of establishing the compositions, crystallographic structures and electronic properties of the last few layers of adsorbents and catalysts – or sub-monolayer amounts of adsorbed species-have been devised thanks largely to the arrival of new techniques such as photoelectron and Auger spectroscopy, and the extension of more traditional ones such as infrared spectroscopy.

In this chapter, we will encounter different chemicals used; methods of preparation and various techniques adopted for structural characterization of catalysts and discuss its capabilities and limitations.
2.1 INTRODUCTION

The majority of heterogeneous catalysts are highly complex composites, usually poorly characterized and not readily characterizable. A mixture of inspiration, science, technology and empiricism is used in their design and development. Their purpose is to bring about, as rapidly as possible, a desired conversion of the reactants, while minimizing the rates at which these substances undergo other reactions, yet in most cases the mechanisms of the desired and unwanted reactions are understood in broad outline only [1]. Characterization is a central aspect of catalyst development [2, 3]. The elucidation of the structures, compositions, and chemical properties of both the solids used in heterogeneous catalysis and the adsorbates and intermediates present on the surfaces of the catalysts during reaction is vital for a better understanding of the relationship between catalyst properties and catalytic performance. This knowledge is essential to develop more active, selective, and durable catalysts, and also to optimize reaction conditions [4]. In this chapter, we come upon some techniques for characterizing catalysts and discuss their capabilities and limitations. These techniques can be broadly grouped according to the nature of the probes employed for excitation, including photons, electrons, ions, and neutrons, or, alternatively, according to the type of information they provide. Here we have chosen to group the main catalyst characterization techniques by using a combination of both criteria into structural, thermal, optical, and surface-sensitive techniques.
Chapter 2

2.2 CHEMICALS FOR CATALYST PREPARATION

The chemicals used for the preparation of catalysts are listed below in Table 2.1.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemicals</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cr(NO₃)₃·9H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>2.</td>
<td>Mn(NO₃)₂·4H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>3.</td>
<td>Fe(NO₃)₃·9H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>4.</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>5.</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>6.</td>
<td>Cu(NO₃)₂·3H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>7.</td>
<td>Polyvinyl alcohol</td>
<td>Merck</td>
</tr>
<tr>
<td>8.</td>
<td>Sucrose</td>
<td>Merck</td>
</tr>
<tr>
<td>9.</td>
<td>Conc. HNO₃</td>
<td>Merck</td>
</tr>
</tbody>
</table>

2.3 CATALYST PREPARATION

*Sol-Gel Thermolysis*

A novel sol–gel thermolysis process using sucrose as the fuel for combustion process and PVA as the protecting agent as well as secondary fuel synthesized the nano-crystalline spinel type chromites [5]. In a typical synthesis procedure, stoichiometric amounts of desired metal were dissolved in 100 mL distilled water to obtain a mixed metal nitrate solution. The pH of the mixture was adjusted to 1 by adding nitric acid. Then a mixture of PVA
(polyvinyl alcohol) and sucrose (4 mol per unit mole of metal ion) were added to the previous solution under hot conditions to compose the homogeneous precursor solution and the molar ratio of PVA to the total metal ions was fixed to be 2:1. The molecular weight of the PVA used was 1, 25,000. The PVA – sucrose mixture just wraps the metal ions to form the sol. After stirring for 30 min, the solution was heated with constant stirring at 80°C for 6 hours to evaporate the water solvent to produce dark transparent viscous gels. The gels were then dried at 150°C for 2 h to obtain the foamy dark precursor powders of the corresponding chromites. The metal ions formed clusters with the oxide ions and remained embedded in the resulting matrix of the mesoporous carbonaceous material. After grinding, the precursors were successively heated at 550°C for 5 h in a muffle furnace to eliminate the organic contents and the final polycrystalline chromites were obtained.

Role of sucrose and PVA in the preparation route

Only PVA could fulfil the purpose, but due to its graphitization tendency, it was partially replaced by sucrose [5]. The aqueous sucrose (always in excess) solution in presence of nitric acid is oxidized to saccharic acid. The saccharic acid is a very good chelating agent for metal ions. PVA (10–20 mol %) in presence of saccharic acid at ambient temperature (~200°C) undergoes polycondensation (polyesterification) reaction [6]. A schematic representation of this reaction is shown in Fig. 2.1. During heating at 200°C, polycondensation reaction occurs and most of the water molecules are removed, resulting in a high viscous polymeric resin. The utility of the polymeric approach comes from the chemical bonding (complexation) of the
cations in to the polymeric chains and ensures the atomistic distribution of the cations throughout the polymeric network. Further heat-treatment of the polymeric resin (at 200°C) causes charring. It is assumed that the metal ions are homogeneously distributed into the charred mass and oxidized at low external temperatures (480–600°C) to the corresponding nano-crystalline oxides [7].

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}^+ + \text{OH}^- \rightarrow \text{C}_6\text{H}_12\text{O}_6 + \text{C}_6\text{H}_12\text{O}_6
\]

**Fig: 2.1 Chemistry of sucrose process**

### 2.4 CATALYSTS PREPARED

The catalysts prepared for the present work with its symbols are listed in Table 2.2.
### Table 2.2 Notations of the catalysts prepared

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Catalyst Symbol</th>
<th>Catalyst</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CuCr₂O₄</td>
<td></td>
<td>CCr</td>
</tr>
<tr>
<td>2.</td>
<td>Cu₀.₇₅Co₀.₂₅Cr₂O₄</td>
<td>CCoCr-1</td>
<td></td>
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<tr>
<td>3.</td>
<td>Cu₀.₅Co₀.₅Cr₂O₄</td>
<td>CCoCr-2</td>
<td></td>
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<tr>
<td>4.</td>
<td>Cu₀.₂₅Co₀.₇₅Cr₂O₄</td>
<td>CCoCr-3</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>CoCr₂O₄</td>
<td></td>
<td>CoCr</td>
</tr>
<tr>
<td>6.</td>
<td>CuFe₀.₅Cr₁.₅O₄</td>
<td>CFCr-1</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>CuFeCrO₄</td>
<td></td>
<td>CFCr-2</td>
</tr>
<tr>
<td>8.</td>
<td>CuFe₁.₅Cr₀.₅O₄</td>
<td>CFCr-3</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>CuFe₂O₄</td>
<td></td>
<td>CF</td>
</tr>
<tr>
<td>10.</td>
<td>Cu₀.₇₅Mn₀.₂₅Cr₂O₄</td>
<td>CMCr-1</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Cu₀.₅Mn₀.₅Cr₂O₄</td>
<td>CMCr-2</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Cu₀.₂₅Mn₀.₇₅Cr₂O₄</td>
<td>CMCr-3</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>MnCr₂O₄</td>
<td></td>
<td>MCr</td>
</tr>
<tr>
<td>14.</td>
<td>Cu₀.₇₅Ni₀.₂₅Cr₂O₄</td>
<td>CNCr-1</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Cu₀.₅Ni₀.₅Cr₂O₄</td>
<td>CNCr-2</td>
<td></td>
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<tr>
<td>16.</td>
<td>Cu₀.₂₅Ni₀.₇₅Cr₂O₄</td>
<td>CNCr-3</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>NiCr₂O₄</td>
<td></td>
<td>NCr</td>
</tr>
<tr>
<td>18.</td>
<td>FeCr₂O₄</td>
<td></td>
<td>FCr</td>
</tr>
</tbody>
</table>

### 2.5 CHARACTERIZATION TECHNIQUES

Catalyst characterization is a lively and highly relevant discipline in catalysis. The ultimate goal of catalyst characterization is to look at the surface
atom by atom, and under reaction conditions. The industrial view on catalyst characterization emphasizes on developing an active, selective, stable and mechanical robust catalyst [8]. Numerous tools are available to explore fundamental relations between the state of a catalyst and its catalytic properties.

Several spectroscopic, microscopic and diffraction techniques are used to investigate catalysts. As Fig. 2.2 illustrates, such techniques are based on some type of excitation (in-going arrows in Fig. 2.2) to which the catalyst responds (symbolized by the outgoing arrows) [9].

Fig. 2.2. Catalyst characterization techniques: The circle represents the sample under study, the inward arrows denote excitation processes, and the outward arrows indicate how the information should be extracted.
2.6 STRUCTURAL TECHNIQUES

2.6.1 Powder X-ray diffraction

X-ray diffraction is one of the oldest and most frequently applied techniques in catalyst characterization. Powder X-ray diffraction (XRD) is a standard method for the characterization of polycrystalline solids to identify crystalline phases inside catalysts by means of lattice structural parameters, and to obtain an indication of particle size. In catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases that are present in the catalyst [9]. Monochromatic X-rays, incident on a polycrystalline sample, are diffracted in all possible directions (as governed by the Bragg equation) simultaneously. Each lattice spacing in the crystal gives rise to a cone of diffraction. Each cone is a set of closely spaced dots, where each dot represents diffraction from a single crystallite within the sample. With a large number of crystallites, these join together form a continuous cone [10].

For a maximum to occur in the diffraction pattern at a particular angle of incidence $\theta$ (with respect to lattice planes (hkl), the Bragg equation must be satisfied:

$$n\lambda = 2 d_{hkl} \sin \theta_{hkl}$$

where $d_{hkl}$-interplanar distance between (hkl) planes, n-order of diffraction and $\lambda =$ wavelength of incident X-rays

X-ray diffraction can also be used to estimate the average crystallite or grain size of catalysts and become broader for crystallite sizes below about 100
nm. Average particle sizes below about 60 nm can be roughly estimated by applying the Scherrer equation,

\[ L = \frac{(0.9 \lambda 180)}{(\pi \beta_{hkl} \cos \theta)} \]

where \( \beta_{hkl} \) is the full width at half-maximum of an \( hkl \) peak at \( \theta \) value.

The XRD peaks are intense and sharp only if the sample has sufficient long-range order. The strength of XRD for catalyst characterization is that it gives clear and unequivocal structure information on particles that are sufficiently large, along with an estimate of their size, and it can reveal this information under reaction conditions. The limitation of XRD is that it can not detect particles that are either too small or amorphous. Hence, one can never be sure that there is no other phases present than the ones detected with XRD. In particular, the surface, where catalytic activity resides, is invisible in standard XRD [9].

Powder X-ray diffraction data were recorded using Bruker AXS D8 Advance X-ray Diffractometer Ni filtered Cu K\( \alpha \) radiation source (\( \lambda = 1.5406 \text{Å} \)) by recording \( \theta \) in the range of 5-80° at a scan rate of 2 °C/min.

2.6.2 Scanning electron microscopy

In scanning electron microscopy (SEM), the yield of either secondary or back-scattered electrons is recorded as a function of the position of the
primary electron beam, and the contrast of the signal used to determine the morphology of the surface: the parts facing the detector appear brighter than those pointing away from the detector [11]. SEM can be used to image over a very large magnification range from 1µm to 100µm, allowing examination of the topology of catalyst surfaces and the morphology of particles and crystals [10,12].

Secondary electron images were obtained on JSM-840 A (Oxford Instruments) scanning electron microscope connected to a 4-quadrant backscattered electron detector under a resolution of 1.38 eV coated with a layer of gold to minimum charge effects.

2.6.3 Energy dispersive X-ray analysis

The elemental analysis of catalysts was determined using energy dispersive X-ray analyzer (EDX). This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20 k eV. This causes X-rays to be emitted from the point of the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth. By moving the electron beam across the material an image of each element in the sample can be acquired. The detector used in EDX is the Lithium drifted Silicon detector. This detector must be operated at liquid nitrogen temperature. When an X-ray strikes the detector, it will generate a photoelectron within the body of the Si, as this photoelectron travels through the Si, it generates electron-hole pairs. The electrons and holes
are attracted to opposite ends of the detector with the aid of a strong electric field. The size of the current pulse thus generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination. A Beryllium window often protects the Si-Li detector. The absorption of the soft X-rays by Be precludes the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced [13]. The chemical compositions of catalysts were obtained from Stereoscan 440 Cambridge, UK energy dispersive X-ray analyzer used in conjunction with SEM.

2.6.4 Transmission Electron Microscopy

The current literature on TEM in catalysis is vast, and forms a rich source of inspiration for many investigators in the field [14-18]. The transmission electron microscope (TEM) has become the premier tool for the microstructural characterization of materials [19]. Transmission electron microscopy (TEM) resembles optical microscopy, except that electromagnetic instead of optical lenses are used to focus an electron beam on the sample. In TEM, a primary electron beam of high energy and high intensity passes through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and the thickness, the transmitted electrons form a two-dimensional projection of the sample mass,
which is subsequently magnified by the electron optics to produce a so-called bright-field image. The dark-field image is obtained from the diffracted electron beams, which are slightly off-angle from the transmitted beam. Very useful results often follow from simple bright field and dark field images without detailed interpretation of image contrast [1]. A combination of topographic and crystallographic information, including particle size distributions, can be obtained in this way. TEM belongs to the most often-used techniques for the characterization of catalysts. The determination of particle sizes or of distributions therein has become a matter of routine, although the results rest of course on the assumption that the size of the imaged particle is truly proportional to the size of the actual particle, and that the detection probability is the same for all particles, independent of their dimensions [8].

A great advantage of the transmission electron microscope is in the capability to observe, by adjusting the electron lenses, both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region. By inserting a selected area aperture and using the parallel incident beam illumination, we get a diffraction pattern from a specific area as small as 100 nm in diameter. Because a selected area diffraction pattern can be recorded from almost every grain in a polycrystalline material, reciprocal lattices (=crystal structures) and mutual crystal orientation relationships can be easily obtained [20].

To study the surface morphology, particle size, and selected area electron diffraction (SAED) of the sol-gel thermolysed samples, transmission
electron microscopy (TEM) (model Phillips Technai-12, FEI, Netherlands) was employed with acceleration voltage 120 kV in bright field mode.

2.6.5 X-ray Fluorescence Analysis

X-ray fluorescence (XRF) analysis is a powerful analytical tool for the spectrochemical determination of almost all the elements present in a sample. XRF radiation is induced when photons of sufficiently high energy, emitted from an X-ray source, impinge on a material. These primary X-rays undergo interaction processes with the analyte atoms. High-energy photons induce ionization of inner shell electrons by the photoelectric effect and thus electron vacancies in inner shells (K, L, M ...) are created. The prompt transition of outer shell electrons into these vacancies within some 100 fs can cause the emission of characteristic fluorescence radiation. Not all transitions from outer shells or subshells are allowed, only those obeying the selection rules for electric dipole radiation. The creation of a vacancy in a particular shell results in a cascade of electron transitions, all correlated with the emission of photons with a well-defined energy corresponding to the difference in energy between the atomic shells involved. The family of characteristic X-rays from each element including all transitions allows the identification of the element. Next to this radiative form of relaxation, a competing process can take place: the emission of Auger electrons. Both processes have Z-dependent probabilities that are complementary: the Auger yield is high for light elements and the fluorescence yield is high for heavy elements.
The working principle of XRF analysis is the measurement of wavelength or energy and intensity of the characteristic photons emitted from the sample. This allows the identification of the elements present in the analyte and the determination of their mass or concentration. All the information for the analysis is stored in the measured spectrum, which is a line spectrum with all characteristic lines superimposed above a certain fluctuating background. Other interaction processes, mainly the elastic and inelastic scattering of the primary radiation on sample and substrate, induce the background.

The most striking feature of XRF analysis is that this technique allows the qualitative and quantitative analysis of almost all the elements (Be-U) in an unknown sample. The analysis is, in principle, non-destructive, has high precision and accuracy, has simultaneous multi-element capacity and requires only a short irradiation time so that a high sample throughput is possible; online analysis is also possible and the running costs are low. The technique is extremely versatile for applications in many fields of science, research and quality control, has low detection limits and a large dynamic range of concentrations covering up to 9 orders of magnitude.

In contrast to all these attractive properties there are some disadvantages. The absorption effects of the primary radiation and the fluorescence radiation created in the analyte result in a shallow layer a few tenths of a millimeter deep that provides information on its composition [21].
The solid samples were simply placed into the sample holder and analysed semi quantitatively using a MiniPal 2 EDXRF (Energy Disperse XRF) Spectrometer.

2.7 ADSORPTION–DESORPTION AND THERMAL TECHNIQUES

2.7.1 BET surface area

Brunauer Emmett and Teller developed the famous BET equation for the determination of the surface area of a solid [22]. The method is based on non-specific physisorption of a gas (N\(_2\) or Ar) onto a solid close to the condensation temperature of the adsorbing gas. Adsorption is characterized by an isotherm, which represents the equilibrium amount of gas adsorbed on a solid at a given temperature as a function of pressure. The BET equation extends the Langmuir isotherm to multilayer adsorption,

\[ \frac{P}{V} \left( \frac{P_0 - P}{P} \right) = \frac{1}{V_m C} + \frac{(C-1)P}{CV_m P_0} \]

where \(V\): the volume, reduced standard conditions (STP) of gas adsorbed per unit mass of adsorbent at a given pressure, \(P\) and constant temperature, \(P_0\); the saturation pressure at the measurement temperature, \(V_m\): volume of gas adsorbed at STP per unit mass of adsorbent, when the surface is covered by a unimolecular layer of adsorbate, and \(C\): a constant, related to the free energy of adsorption.
According to this equation, a plot of $P/V (P_0 - P)$ versus $P/P_0$ should yield a straight line. The surface area is then calculated using:

$$S_{\text{BET}} = V_m A_m N_a / V_{\text{mol}}$$

where $N_a$: Avogadro's number $(6.0238 \times 10^{23})$, $V_{\text{mol}}$: molar volume of absorbate gas at STP $(22.41 \text{mol}^{-1})$ and $A_m$: Cross sectional area of adsorbed gas, $A_m (N_2) = 0.162 \text{ nm}^2$. When nitrogen is the adsorbing gas this reduces to:

$$S_{\text{BET}} = 4.353 V_m$$

The BET surface areas of samples were measured using Micromeritics Tristar 3000 surface area analyzer. The samples were activated at $500^\circ \text{C}$ for $1\text{h}$ before the analysis and then degassed at $350^\circ \text{C}$ for $3\text{h}$ under nitrogen flow.

### 2.7.2 Temperature programmed desorption-$\text{NH}_3$

Temperature-programmed desorption (TPD) – which is also referred to as thermal desorption spectroscopy (TDS) – can be used on technical catalysts, but is particularly useful in surface science, where the desorption of gases from single crystals and polycrystalline foils into vacuum is examined [23]. Temperature-programmed desorption (TPD) in particular is often employed to obtain information about specific sites in catalysts [21, 22]. The temperature at which desorption occurs indicates the strength of adsorption, whereas either the amount of gas consumed in the uptake or the amount of desorption upon
heating attests to the concentration of the surface sites. The most common molecules used in TPD are NH₃ and CO₂, which probe acidic and basic sites, respectively, but experiments with pyridine, O₂, H₂, CO, H₂O, and other molecules are often performed as well [24-26]. In this, an inert gas is passed over a catalyst bed, while the temperature is increased. A TPD profile is obtained by monitoring the gases, which are desorbed from the surface as the temperature is increased. The temperature of desorption is an indication of the strength of binding of the adsorbate [27]. The analysis of TPD spectra is a time-consuming matter, if it is to be performed correctly!

Acidity measurements were performed by temperature programmed desorption (TPD-NH₃) of ammonia using a conventional flow apparatus. In a typical experiment, about 500 mg of catalyst was activated at 773 K for 1 h and kept in a tube. The sample was pretreated by passage of nitrogen at 573 K for 1 h. Subsequently catalyst was saturated with pure anhydrous ammonia gas and the system was allowed to attain equilibrium. After 30 min, the excess and physisorbed ammonia was subsequently flushed with flowing nitrogen. TPD analysis was then carried out by desorption of ammonia from 373 to 873 (K) at a heating rate of 293 K/min in nitrogen atmosphere and trapped in H₂SO₄. The amount of ammonia desorbed is calculated by titrating against NaOH.

2.7.3 Thermal analysis

2.7.3.1 TG/DTG/DTA analysis

Changes in catalysts during preparation, which often involves thermal calcination, oxidation, and reduction, can also be followed by recording the
associated variations in sample weight, as in normal thermogravimetry (TG) or
differential thermogravimetry (DTG); or in sample temperature, as in
differential thermal analysis (DTA) [28-30]. Although these thermal methods
are quite traditional, they are still used often in catalysis research.
Thermogravimetric analysis (TGA) provides a quantitative measurement of
any weight changes associated with thermally induced transitions. It can record
directly the loss in weight as a function of temperature or time [31]. In TGA,
the weight of sample is continuously recorded as the temperature is increased.
Samples are placed in a crucible that is positioned in a furnace on a quartz
beam attached to an automatic recording balance. The horizontal quartz beam
is maintained in the null position by the current flowing through the transducer
coil of an electromagnetic balance. Any change in the weight of the sample
causes a deflection of the beam, which is sensed by one of the photodiodes
connected to act as a position sensor to determine the movement of the beam.
The beam is then restored to the original null position by a feedback current
sent from the photodiodes to the coil of the balance and the current is
proportional to the change in weight of the sample. In differential thermal
analysis (DTA), the difference in temperature between the sample and a
thermally inert reference material is measured as a function of temperature
usually the sample temperature. Any transition that the sample undergoes
results in liberation or absorption of energy by the sample with a

corresponding deviation of its temperature from that of the reference. A plot of
the differential temperature, \( \Delta T \), versus the programmed temperature, \( T \),
indicates the transition temperatures and whether the transition is exothermic
or endothermic. When an endothermic change occurs, the sample temperature
lags behind the reference temperature because of the heat in the sample. Exothermic behaviour is associated with the decrease in enthalpy of a phase or a chemical system. DTA and thermogravimetric analyses are often run simultaneously on a single sample.

Besides the prediction of calcination temperatures during catalyst preparation, thermal analysis is also used to determine the composition of catalysts based on weight changes and thermal behaviour during thermal decomposition and reduction, to characterize the aging and deactivation mechanisms of catalysts, and to investigate the acid–base properties of solid catalysts using probe molecules. However, these techniques lack chemical specificity, and require corroboration by other characterization methods.

Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were performed with a Perkin Elmer Pyris Diamond TG/DTA Analyzer under nitrogen atmosphere at heating rate of 10°C/min from room temperature to 800°C with samples mounted on a platinum sample holder.

2.7.3.2 TGA adsorption studies

The catalyst samples activated at 500°C for 2h were kept in two different desiccators saturated with pyridine, and 2,6-dimethylpyridine (2,6-DMP) vapours respectively. For the effective and uniform adsorption the samples were kept inside the desiccator for 48 h. After this, the weight loss of the adsorbed samples was measured by thermogravimetric analysis operating
between 40 to 600°C at a rate of 20°C/minute. For the pyridine adsorbed samples, the weight loss between 100-200°C, 201-400°C and 401-600°C are considered to be measures of weak, medium and strong acid sites, respectively. Since the 2,6-DMP weakly bound to Lewis acid sites get desorbed below 300°C, the weight loss between 301-400°C, 401-500°C and 501-600°C are considered to be measures of weak, medium and strong acid sites, respectively.

2.8 OPTICAL SPECTROSCOPIES

2.8.1 FT-Infrared spectroscopy

In catalysis, infrared (IR) spectroscopy is commonly used to characterize specific adsorbates. Because of the localized nature and particular chemical specificity of molecular vibrations, IR spectra are quite rich in information, and can be used to extract or infer both structural and compositional information on the adsorbate itself as well as on its coordination on the surface of the catalyst. In some instances, IR spectroscopy is also suitable for the direct characterization of solids, especially if they can be probed in the far-IR region (10–200 cm⁻¹) [32-34]. Every chemical compound has its own characteristic IR spectrum.

Several working modes are available for IR spectroscopy studies [32-34]. The most common arrangement is transmission, where a thin solid sample is placed between the IR beam and the detector; this mode works best with weakly absorbing samples. Using the so-called transmission technique the catalyst powder is compressed and used as a self-supporting disc.
Unfortunately, the necessary high pressure can cause phase transitions within the disc and thus leads to misinterpretations. Furthermore, using discs that are too thick can result in total absorption of the IR radiation by the catalyst material. These disadvantages are overcome by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), where pure catalyst powders can be analysed without any previous mechanical manipulation. Many substances in their natural states (e.g., powders and rough surface solids) exhibit diffuse reflection, i.e., incident light is scattered in all directions as opposed to specular (mirror-like) reflection where the angle of incidence equals the angle of reflection. These spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components as well as scattering phenomena in the collected radiation.

Diffuse reflection accessories are commercially available. They collect the diffusely scattered IR radiation by means of large ellipsoid mirrors. Even the largest mirrors only permit the collection of a part of the scattered radiation; therefore the use of diffuse reflection accessories is restricted to FT-IR spectrometers (diffuse reflection in IR by FT spectrometer – DRIFT). The Kubelka-Munk transformation has to be performed in order to linearize the ordinate of the obtained spectra. Integrating spheres (so-called Ulbricht spheres) are no longer used in MIR due to the lack of non-absorbing and uniformly high-scattering coatings for the inside of the sphere.

The applications of IR spectroscopy in catalysis are many. IR can be used to directly characterize the catalysts themselves. Further catalyst
characterization can be carried out by appropriate use of selected adsorbing probes.

Owing to its great molecular specificity, good sensitivity, and high versatility, IR spectroscopy is one of the most widely used techniques for catalyst characterization. Nevertheless, IR catalytic studies do suffer from a few limitations. In particular, strong absorption of radiation by the solid often limits the vibrational energy window available for analysis. Also, the intensities of IR absorption bands are difficult to use for quantitative analysis. Finally, it is not always straightforward to interpret IR spectra, especially in cases involving complex molecules with a large number of vibrational modes.

The IR spectra were recorded through JASCO’s FTIR-4000 series spectrometer in the MIR range (4000 cm\(^{-1}\) to 400 cm\(^{-1}\)) in DRIFT mode.

2.8.2 Infrared adsorption studies

The exposed cations and anions on oxide surfaces have been described as acid-base site pairs [35,36]. The oxygen anions can act as Bronsted or Lewis base sites; the metal cations are Lewis acid sites. Hydroxyl groups bound at certain oxide surfaces may exhibit considerable Bronsted acidity, but by and large we can neglect Bronsted acidity of oxide surfaces in surface science studies. Strong Bronsted acidity usually arises in mixed oxides rather than pure oxides, due to charge imbalances and/or coordination changes caused by incorporation of a second cation type [37,38].
A variety of physico chemical methods have been employed and widely applied to evaluate the strength and the amount of acid sites on catalysts. A large variety of probe molecules have been utilized to both qualitatively ascertain the acidity and provide the measure and nature of these acidic sites [39-46]. For example, pyridine was chosen as the base probe molecule to measure the acidity. When chemisorbed on a surface possessing acid properties, pyridine can interact with acidic protons, electron acceptor sites and H from neutral or weakly acidic hydroxyls [43,44].

The acid–base properties of specific surface sites can be tested by recording the ensuing vibrational perturbations and molecular symmetry lowering of either acidic (CO and CO$_2$) or basic (pyridine and ammonia) adsorbates. Oxidation states can also be probed by using carbon monoxide [47,48].

The catalyst samples activated at 500°C for 2h were kept in two different desiccators saturated with pyridine, and 2,6 – dimethylpyridine (2,6-DMP) vapours respectively. For the effective and uniform adsorption the samples were kept inside the desiccator for 48 h. The IR spectra were recorded through JASCO's FTIR-4000 series spectrometer in the MIR range (4000 cm$^{-1}$ to $400 \text{ cm}^{-1}$) in DRIFT mode.
2.8.3 UV-vis Diffused reflectance spectroscopy

Many materials undergo electronic transitions upon heating which can be studied by UV-Vis spectroscopy. Most often, the samples studied by this method are liquids. Analysis of powders and other solids is less straightforward, unless they can be dissolved and measured as a liquid. For non-soluble solids, the only feasible methods for such analysis in the UV-Vis are specular reflectance and diffuse reflectance. The former is suitable for highly reflective materials; the latter for powders and roughened solids.

Diffuse reflectance spectroscopy (DRS) is a spectroscopic technique based on the reflection of light in the ultraviolet (UV), visible (VIS) and near-infrared (NIR) region by a powdered sample. In a DRS spectrum, the ratio of the light scattered from an “infinitely thick” closely packed catalyst layer and the scattered light from an infinitely thick layer of an ideal non-absorbing (white) reference sample is measured as a function of the wavelength $\lambda$. The scattered radiation, emanating from the sample, is collected in an integration sphere and detected.

The main drawback of the use of UV-Vis spectroscopy for catalyst characterization is that the data commonly show broad and overlapping absorption bands with little chemical specificity. Also, it is often quite difficult to properly interpret the resulting spectra.
UV-vis DR spectra for the initial determination of the oxidation state of the transition metals were taken in the range 200-900nm on a Spectro UV-VIS DOUBLE BEAM UVD-500 spectrometer. The spectra were recorded at room temperature using MgO as a reference. Prior to measurement, the samples were pretreated for 1h at the calcinations temperature.

2.9 SURFACE-SENSITIVE SPECTROSCOPY

2.9.1 X-ray Photoelectron Spectroscopy (XPS)

(XPS), also known as electron spectroscopy for chemical analysis (ESCA), is one of the most powerful and common chemical analysis techniques. XPS is based on the photoelectric effect in which the binding energy ($E_B$) of a core level electron is overcome by the energy ($hv$) of an impinging soft X-ray photon, and the core-level electron is excited and ejected from the analyte. The kinetic energies of the ejected photoelectrons, $E_K$, are measured by an electron spectrometer whose work function is $\varphi$. Invoking conservation of energy, the following relationship is obtained:

$$E_B = hv - E_K - \varphi$$

The binding energy of the photoelectron is characteristic of the orbital from which the photoelectron originates. The binding energy of the ejected photoelectron depends on the final state configuration after photoemission. The final state is characterized by full relaxation of all atomic orbitals towards the hole in the core level [37].
Shake-up peaks may occur when the outgoing photoelectron simultaneously interacts with a valence electron and excites it (shakes it up) to a higher-energy level. The kinetic energy of the core electron is then slightly reduced giving a satellite structure a few eV below (above on the binding energy scale) the core level position [38].

A general ingredient of core level spectroscopies is the core hole spin-orbit splitting. The coupling of the orbit and spin angular momenta is given by the spin-orbit interaction, which is essentially a relativistic effect. The spin-orbit interaction is very large for core holes and in general two peaks or structures will be visible in the spectrum, separated by the core hole spin-orbit splitting. The intensity ratio of $2p_{1/2}$ versus $2p_{3/2}$ peak is 1:2. and that of $3d_{3/2}$ to $3d_{5/2}$ peak is 2:3. This rule breaks down if there are other interactions, which are able to mix the spin-orbit split states. The charge-transfer effect plays a major role in XPS. More drastic charge-transfer effects were observed in f and d electron systems where charge transfer occurs from conduction (or valence) band states to the f or d electron states in order to screen the core-hole potential. This causes a splitting of the XPS spectra into well-screened and poorly screened final states. The multiplet coupling effect plays a minor role in the XPS process compared to that of the charge-transfer effect [39].

The measurement is carried out in an UHV chamber. Monochromatic X-ray photons, typically from an Al-Kα (1486.6 eV) or Mg-Kα (1253.6 eV) X-ray source, are shone at the sample to eject photoelectrons. These electrons have energies ranging from 0 eV up to almost the same energy as the incident photons but most are emitted at a few discrete energies that are characteristic
of the elements present in the sample. The photoelectrons are collected by an electron energy analyser such as a hemispherical mirror analyser (HMA) to produce a spectrum of the number of electrons vs. their kinetic energy. Analysis of this spectrum provides quantitative information about the composition of the near surface region of the sample [16].

The XPS were performed on Kratos Axis 165 X-ray photoelectron spectrometer equipped with dual Al-Mg anodes interfaced with the necessary data handling software. For all catalysts prepared the spectra were recorded under ultrahigh vacuum conditions (10^{-9} Torr), using Al K\(\alpha\) primary radiation (15 kV, 5 mA) operated at 150W. Each analysis started with a survey scan from 0 to 1200 eV with a dwell time of 100 milliseconds, pass energy of 160 eV at steps of 1eV with one sweep. For the high-resolution analysis, the number of sweeps was increased, the pass energy was lowered to 80eV at steps of 100 meV and the dwell time was changed to 250 milliseconds. The spectra were charge corrected using the advantageous C 1s signal at 284.6 eV. The relative intensities of the surface composition of different elements were corrected with their corresponding atomic sensitivity factors using the vision two software in unix system. Prior to the XPS studies, all the catalysts were reduced in 6% H\(_2\) balance He flow at 523K for 4 h, followed by passivation in N\(_2\) atmosphere.
REFERENCES

[22] B.K Hodnett, “Heterogeneous Catalytic Oxidation: Fundamental and
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