Chapter 2

Preparation and characterization of zirconia-supported heteropoly acid catalysts

2.1. Introduction

The successful heterogeneous catalysts should possess high catalytic activity for the desired reaction, high selectivity for the desired product and acceptable commercial life. The characterization of catalytic material is a very important step in the process of catalyst development, which gives insight into the relation between physical and chemical properties of the catalyst and its activity. If the structure and composition of the catalyst can be correlated with its activity and selectivity, the working of the catalyst can be understood.

In this work, the catalysts were prepared by impregnation method and characterized by various techniques such as surface area, X-ray diffraction, Raman spectroscopy, TG-DTA, XPS, FTIR pyridine adsorption, TPD of ammonia, DRUV-vis spectroscopy, NMR etc. The theory and experimental procedure of various characterization techniques used are briefly described in the following sections.

2.2. Catalyst preparation

The catalysts were prepared by suspending a known amount of dried zirconium oxyhydroxide powder in a methanol solution of heteropoly acids (HPAs). HPAs (Aldrich) under study include silicotungstic acid, phosphotungstic acid and phosphomolybdic acid. Zirconium oxyhydroxide was prepared by the hydrolysis of 0.5 M zirconyl chloride solution by the drop wise addition of aqueous ammonia (10 M) to a final pH of 10. The precipitate was filtered and washed with ammoniacal water (pH = 8) until free from chloride ions by the silver nitrate test. Zirconium oxyhydroxide thus obtained was dried at 120 °C for 12 h, powdered well and dried again for another 12 h. Each time, 4 ml of methanol per gram of solid support was used and the mixture was stirred in a rotary evaporator for 8-10 h. After stirring, the excess methanol was removed.
at ca. 50 °C under vacuum. The resulting solid materials were dried at 120 °C for 24 h and ground well. A series of catalysts with different HPA loading were prepared by changing the HPA concentration in methanol. The dried samples were then calcined in air. All samples were calcined in shallow quartz boats placed inside a 3 cm diameter quartz tube placed in a tubular furnace. The samples were heated at the rate of 5 °C min⁻¹ to the specified temperature and held for 4 h under static conditions, and then cooled at the rate of 5 °C min⁻¹ to room temperature.

2.3. Catalyst characterization – Theory and experimental procedure

2.3.1. Surface area measurement by BET method

The common method of measuring surface area of catalyst materials is based on the theory developed by Brunauer, Emmett and Teller in 1938 considering the concept of multilayer adsorption. The isotherm points are transformed into the linear version of BET equation [1]:

\[ \frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)/V_mC}{P/P_0} \]  

(2.1)

Where,

- \( P \) is the adsorption equilibrium pressure,
- \( P_0 \) is the saturation vapor pressure of the adsorbate at the experimental temperature,
- \( V \) is the volume of gas adsorbed at pressure \( P \),
- \( V_m \) is the volume of adsorbate required for monolayer coverage and \( C \), a constant that is related to the heat of adsorption and liquefaction. A plot of \( P/V(P_0-P) \) Vs \( P/P_0 \) will yield a straight line usually in the range \( 0.05 < P/P_0 < 0.35 \). The monolayer volume, \( V_m \) is given by \( 1/(S+1) \), where \( S \) is the slope, which is equal to \( (C-1)/V_mC \) and \( I \) is the intercept, which is equal to \( 1/V_mC \). The surface area of the catalyst (\( S_{BET} \)) is related to \( V_m \) by the equation,

\[ S_{BET} = \frac{V_m}{22414} N_a \sigma \]  

(2.2)

where, \( N_a \) is the Avogadro number and \( \sigma \) is mean cross sectional area covered by one adsorbate molecule. The \( \sigma \) value generally used for \( N_2 \) is 0.162 nm².

The specific surface area of the catalysts were measured by \( N_2 \) physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multi point BET analysis method. Zirconia-supported silicotungstic acid samples were dried in flowing \( N_2 \), while zirconia-supported phosphotungstic acid
samples were dried under dynamic vacuum for 2 h at 300 °C before N₂ physisorption measurements.

2.3.2. X-ray diffraction

X-ray diffraction (XRD) is used to identify bulk phases, if desired under in situ conditions and to estimate particle sizes. In catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases that are present in the catalyst [2]. This method involves the interaction between the incident monochromatized X-rays (like Cu Kα or Mo Kα source) with the atoms of a periodic lattice. X-rays scattered by atoms in an ordered lattice interfere constructively in directions given by Bragg’s law:

$$ n\lambda = 2d \sin \theta; \quad n = 1, 2, 3, \ldots \quad (2.3) $$

Where, \( \lambda \) is the wavelength of the X-rays, \( d \) is the distance between two lattice planes, \( \theta \) is the angle between the incoming X-rays and the normal to the reflecting lattice plane and \( n \) is the integer called order of the reflection.

The Bragg peaks are measured by observing the intensity of the scattered radiation as a function of scattering angle \( \theta \). The angles of maximum intensity enable one to calculate the spacing between the lattice planes and allow phase identification. The width of diffraction peaks provides information on the dimensions of the reflecting planes. Diffraction lines from the perfect crystals are very narrow. For crystals with size below 100 nm, line broadening occurs due to incomplete destructive interference in scattering directions, where the X-rays are out of phase. The width of the diffraction lines can be used to estimate the crystal size by the relation, Debye-Scherrer formula [1],

$$ D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta} \quad (2.4) $$

where, \( D_{hkl} \), \( \lambda \), \( \beta \) and \( \theta \) are the volume averaged particle diameter, X-ray wavelength, full width at half maximum (FWHM), and diffraction angle respectively.

A major limitation of XRD is that this technique requires samples possessing sufficient long-range order. Amorphous phases and small particles give either broad and weak diffraction lines or no diffraction at all which makes them virtually invisible for XRD.

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered CuKα radiation (\( \lambda = \)

---

*Chapter 2: Preparation and characterization of zirconia-supported heteropoly acid catalysts*
1.5418 Å). The volume percentage of the tetragonal phase ($V_t$) of the calcined samples was estimated using the formula proposed by Toraya et al. [3],

$$X_m = I_m (11-1) + I_m (111)/[I_m (11-1) + I_m (111) + I_t (111)]$$  \hspace{1cm} (2.5)

$$V_m = 1.311 X_m / [1 + 0.31 X_m]$$ \hspace{1cm} and $V_t = 1 - V_m$  \hspace{1cm} (2.6)

where, $I_m$ (hkl) is the integral intensity of the (hkl) reflections of the monoclinic phase and $I_t$ (111) the intensity of the (111) reflection of the tetragonal phase.

2.3.3. Raman spectroscopy

Raman spectroscopy is based on the inelastic scattering of photons, which loose energy by exciting vibrations in the sample. A vibration is Raman active if it changes the polarizability of the molecule. Raman and infrared spectroscopies complement each other, in particular for highly symmetrical molecules.

Raman spectroscopy can be used for investigations of oxides, supported and bulk metals, and has found increasing applications for the characterization of supported transition metal oxide catalysts since the work of Villa et al. in 1974 [4]. It is particularly powerful for investigations of the structure of supported oxide catalysts. All characteristic vibrational features of oxides of the transition metals like Mo, W, Cr, V and Re fall into the frequency range below 1100 cm$^{-1}$. These oxides have high Raman scattering cross-sections because of their relatively high covalent bond character. The usual support materials (particularly alumina and silica) have very low Raman scattering cross-sections and only show weak absorption bands in the 700-1100 cm$^{-1}$ region. Hence, it has the advantage that the normal modes of the minority components, namely the transition metal oxides dispersed on the supports, can most frequently be detected by it with relative ease in the frequency region 500-1000 cm$^{-1}$. It should be also mentioned that titania and zirconia oxides possess strong Raman absorption bands in the region below 700 cm$^{-1}$. There are some major problems that may be encountered in it like the heating effects of the laser beam, low sensitivity of the technique and background fluorescence.

Raman spectra of the catalysts were recorded on powder samples at room temperature with a Bruker IFS 66 spectrometer connected to Raman module FRA 106. The 1.06 μm line of NdYAG laser was used for excitation and spectral resolution was 3 cm$^{-1}$. 

33
2.3.4. Thermal analysis

Thermo analytical techniques involve the measurement of the response of the solid under study (energy or mass released or consumed) as a function of temperature (or time) dynamically by the application of a linear temperature program. Thermogravimetry (TG) is a technique, which measures the variation in mass of a sample when it undergoes temperature scanning in a controlled atmosphere. Differential thermal analysis (DTA) is a technique, which measures the difference in temperature between a sample and a reference (a thermally inert material) as a function of time or temperature, when they undergo temperature scanning in a controlled atmosphere. DTA method enables any transformation to be detected for all the categories of materials, providing information on exothermic and endothermic reactions taking place in the sample, which include phase transitions, dehydration, decomposition, redox, or solid-state reactions. In catalysis, these techniques are used to study the genesis of catalytic materials via solid-state reactions.

Differential thermal analysis (DTA) measurements of zirconia-supported silicotungstic acid samples were performed on a Pyris Diamond TG-DTA apparatus from room temperature to 1000 °C in flowing dry oxygen (ca. 50 ml min⁻¹), using α-Al₂O₃ as reference. In each experiment, 5-8 mg of the sample was used with a heating rate of 20 °C min⁻¹.

Thermogravimetric and differential thermal analysis (TG-DTA) measurements of zirconia-supported phosphotungstic acid samples were performed on a Setaram TG-DTA 92 apparatus from room temperature to 1000 °C in flowing dry air (ca. 50 ml min⁻¹), using α-Al₂O₃ as reference. In each experiment, 25-30 mg of the sample was used with a heating rate of 10 °C min⁻¹. TGA curves are depicted as first derivative DTG of the direct weight loss traces.

2.3.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is one of the most frequently used techniques in catalysis. It gives information on the elemental composition, the oxidation state of the elements and in some cases on the dispersion of one phase over another. XPS is based on the photoelectric effect [5-7]. In this technique, sample surface is irradiated with X rays and the emitted photoelectrons are measured. When an atom absorbs a
photon of energy \(hv\), a core or valence electron with binding energy \(E_b\) is ejected with kinetic energy \(E_k\):

\[
E_k = hv - E_b - \phi
\]

(2.7)

where, \(h\) is Planck's constant, \(v\) is the frequency of the exciting radiation, \(E_b\) is the binding energy of the photoelectron relative to the Fermi level of the sample and \(\phi\) is the work function of the spectrometer.

XPS (also referred by the acronym ESCA, electron spectroscopy for chemical analysis) entails emission from both core and valence electrons of the solid, the stimulating X-ray sources being usually Al Ka (1486.6 eV) or Mg Ka (1253.6 eV). XPS spectrum is a plot of the intensity of photoelectrons Vs binding energy. Since, the electrons whose energies are analyzed in XPS arise from a depth of no greater than about 5 nm, the technique is highly surface specific. A set of binding energies is characteristic for an element and hence XPS can be used to analyze the composition of samples, considering the area of the peak and cross section for photoemission. Binding energies are not only element specific but contain chemical information like oxidation state, because the energy levels of core electrons depend slightly on the chemical state of the atom.

An experimental problem in XPS is that electrically insulating samples may charge during measurement, as photoelectrons leave the sample. Due to the positive charge on the sample, all XPS peaks in the spectrum shift by the same amount to higher binding energies. Calibration for this effect can be done by using C 1s binding energy (284.9 eV) from carbon contamination, which is present in most of the catalysts.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized Mg-K\(\alpha\) X-ray source. Base pressure in the analysis chamber was maintained at 3-6 x 10\(^{-10}\) Torr range. Energy resolution of the spectrometer was set at 0.8 eV with Mg-K\(\alpha\) radiation at a pass energy of 50 eV.
2.3.6. Temperature programmed techniques: TPD of ammonia

Temperature programmed reduction (TPR), oxidation (TPO), desorption (TPD) and reaction spectroscopy (TPRS) typically involves monitoring surface or bulk processes between the solid catalyst and its gaseous environment via continuous analysis of the gas phase composition as the temperature is raised linearly with time. Instrumentation for temperature-programmed investigations consists of a reactor charged with catalyst in a furnace that can be temperature programmed and a thermal conductivity detector (TCD) to measure the concerned active gas of the gas mixture before and after interaction.

The acidity of the catalysts were measured by temperature programmed desorption of NH$_3$ (NH$_3$-TPD) using a micromeritics AutoChem-2910 instrument. It was carried out after ~ 0.5 g of the catalyst sample was dehydrated at 600 °C in helium flow (30 cm$^3$ min$^{-1}$) for 1 h. The temperature was decreased to 100 °C and NH$_3$ was adsorbed by exposing the samples treated in this manner to a stream containing 10 % NH$_3$ in helium for 1 h at 100 °C. It was then flushed with helium for another 1 h to remove physisorbed NH$_3$. The desorption of NH$_3$ was carried out in helium flow (30 cm$^3$ min$^{-1}$) by increasing the temperature to 600 °C at 10 °C min$^{-1}$ measuring NH$_3$ desorption using TCD detector.

For zirconia-supported phosphotungstic acid catalysts, NH$_3$-TPD measurements were carried out after 0.1 g of the catalyst sample was dehydrated at 500 °C in dry air for 1 h and purged with helium for 0.5 h. The temperature was decreased to 125 °C under the flow of helium and then 0.5 ml NH$_3$ pulses were supplied to the samples until no further uptake of ammonia was observed. NH$_3$ was desorbed in helium flow by increasing the temperature to 540 °C at 10 °C min$^{-1}$ measuring NH$_3$ desorption using a TCD detector.

2.3.7. Infrared adsorption studies - Pyridine adsorption

The most common application of IR in catalysis is to identify adsorbed species and to study the way in which these species are chemisorbed on the surface of the catalyst [8-10]. More specifically, IR spectroscopy has been used to study the adsorption of typical probe molecules like ammonia, pyridine and other bases, hydrocarbons, carbon dioxide which can monitor either the acidic or basic sites on oxide catalysts [11].
Investigation of adsorbed species in relation to their behavior in catalytic reactions is the main field of application of IR spectroscopy.

The pyridine adsorption studies were carried out in the DRIFT (diffuse reflectance infrared Fourier transform) mode using a Shimadzu SSU 8000 instrument. A calcined powder sample in a sample holder was placed in a specially designed cell. The samples were then heated \textit{in-situ} from room temperature to 400 °C at a heating rate of 5 °C min\(^{-1}\) in a flowing stream (40 ml min\(^{-1}\)) of pure N\(_2\). The samples were kept at 400 °C for 3 h and cooled to 100 °C and then pyridine vapor (20 \textmu{l}) was introduced under N\(_2\) flow and the IR spectra were recorded at different temperatures up to 400 °C. A resolution of 4 cm\(^{-1}\) was attained after averaging over 500 scans for all the IR spectra reported in this study.

For zirconia-supported phosphotungstic acid (PTA) catalysts with different PTA loading, pyridine adsorption studies were performed using NICOLET MODEL 60 SXB instrument by heating \textit{in-situ} a self-supporting wafer (20 mg) of the sample from room temperature to 400 °C with a heating rate of 5 °C min\(^{-1}\) under vacuum (10\(^{-6}\) mbar). The samples were kept at 400 °C for 3 h followed by cooling to 100 °C. Pyridine vapor (10 mm Hg) was introduced into the cell and allowed to equilibrate for 45 minutes followed by evacuation at 100 °C for 30 minutes and the IR spectrum was recorded. Then the temperature was slowly increased and IR spectra were recorded at different temperatures up to 400 °C.

2.3.8. Diffuse reflectance UV-visible spectroscopy

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 most popular continuum theory describing diffuse reflectance effect is Schuster-Kubelka-Munk (SKM) theory. If the sample is infinitely
thick, the diffuse reflection of the sample \((R_\infty)\) is related to an apparent absorption \((K)\) and apparent scattering coefficient \((S)\) by the SKM equation [12, 13]:

\[
F(R_\infty) = (1-R_\infty)^2 / 2R_\infty = K/S
\]

(2.8)

At low concentrations of supported transition metal ions (TMI), this equation is a good representation of the absorbing spectrum and allows a quantitative determination of the TMI.

\[
F(R_\infty) = (1-R_\infty)^2 / 2R_\infty = K/S = \alpha C_{\text{TMI}} / S = k C_{\text{TMI}}
\]

(2.9)

At a given wavelength \(\lambda\), \(S\) is constant, the above equation gives a linear relation between \(F(R_\infty)\) and the TMI concentration, \(C_{\text{TMI}}\). The coefficients \(\alpha\) and \(k\) are proportionality constants.

DRS is a suitable technique for studying the speciation of supported TMIs because it measures both their d-d transitions and charge transfer bands. The obtained information is directly chemical since the outer shell electrons are probed. The DRS technique can be used under in-situ conditions and can be applied at different levels of sophistication, from detecting the presence of a certain oxidation state of a supported TMI to a detailed distribution of different oxidation states and coordination environments under catalytic conditions.

The disadvantage is that the DRS signals are usually broad and overlap with each other, leading to a biased spectral analysis. In addition, the origin of the specific electronic transition is sometimes difficult to isolate due to its dependence on the local coordination environment, the polymerization degree and the specific oxidation state.

Diffuse reflectance UV-vis (DRUV-vis) spectra of catalyst samples were obtained using a Shimadzu UV-2101 PC spectrometer equipped with a diffuse-reflectance attachment, with BaSO\(_4\) as the reference. The reflectance spectra were converted into the Kubelka-Munk function, \(F(R)\), which is proportional to the absorption coefficient for low values of \(F(R)\). The spectra were measured in the range of 200-800 nm in air at room temperature.

2.3.9. \(^{31}\text{P}\) solid-state nuclear magnetic resonance spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy gives information on the interaction of a nucleus having a nuclear spin quantum number, \(I\), greater than zero with
an external magnetic field. The interaction of nuclear spins with the externally applied
magnetic field, $B_0$, and their environment can be described by the spin Hamiltonian $H$:

$$H = H_z + H_{cs} + H_Q + H_D + H_J$$

(2.10)

$H_z$ is a Hamiltonian, which describes the interaction of the nuclear spin with the external
field $B_0$ (Zeeman interaction). The chemical shift Hamiltonian $H_{cs}$ gives the information
on the local environment of a nucleus. The chemical shift is measured relative to that of a
reference compound and is expressed in Hertz or in ppm with respect to the resonance
frequency of the reference compound. $H_Q$ describes the quadrupolar interaction of the
nucleus with the surrounding electric field gradient. $H_D$ describes the dipolar interaction
with other nuclei, while $H_J$ describes the interaction with other nuclei through J-coupling.

In solid-state NMR, the line shape is determined by dipolar and quadrupolar
interactions. The lines are usually broader because the rigid structure of the solid phase
prevents the averaging of the dipolar interaction ($H_D$) by motions. Since, the first order
quadrupolar and dipolar interactions are proportional to $(3 \cos^2\theta - 1)$, where, $\theta$ is the
angle between an internuclear vector and the magnetic field, these interactions can be
removed, to a first order approximation, by spinning the sample around the so-called
magic angle $\beta$ with respect to the external magnetic field, for which $3 \cos^2\beta - 1 = 0$, i.e. $\beta$
$= 54.74^\circ$. This technique is known as Magic Angle Spinning (MAS) [14, 15].

Phosphorus contains only one isotope, $^{31}P$, with a nuclear spin of $I = 1/2$. This and
the high magnetic moment (which results in a high sensitivity) makes it an interesting
nucleus for NMR spectroscopy. Solid state NMR gives insight into the structure of solids
and enables us to probe the local environment of a nucleus. Unlike X-ray diffraction,
NMR spectroscopy is not restricted to materials with long-range order but can also be
applied to amorphous substances.

The $^{31}P$ MAS NMR spectra were recorded using a Bruker DSX-300 spectrometer
at 121.5 MHz with high power decoupling with a Bruker 4 mm probe head. The spinning
rate was 10 KHz and the delay between two pulses was varied between 1 and 30 s to
ensure the complete relaxation of the $^{31}P$ nuclei occurred. The chemical shifts are given
relative to external 85 % H$_3$PO$_4$. 

39
2.3. References