Solid catalysts

Book: *Chemical Engineering Kinetics*, J. M. Smith, 2nd Edition (Chapter 8), 3rd Edition (Chapter 8)

Catalyst preparation

Mixed agglomerated (co-precipitated) catalyst

- Involves the **co-precipitation** of both **support precursor** and **catalytic species precursor**
- Often used to prepare non-precious metal catalysts

Eg., $Ni(NO_3)_2 + Al(NO_3)_3 + Na_2CO_3 \rightarrow NiCO_3 \downarrow + Al(CO_3)_3 + NaNO_3$

- **Maintaining the pH** is very important in this process – pH determines whether precipitation occurs **simultaneously (desired) or sequentially**
- A **flocculated multi-component precipitate** is formed in which the **catalytic metal microcrystals** are each surrounded by **support precursor crystals**
- The surrounding support crystals **prevent the metal crystals from coming together** and sintering
- Precipitate is then **thoroughly washed**, **filtered**, **dried and calcined** (to form oxides from hydroxides and carbonates)

Catalyst Characterization

Determination of the **physical and chemical characteristics** of the catalyst which are responsible for its performance in a reaction

Physico-chemical properties of catalysts -

1) **Elemental composition** of catalyst
2) **Nature** and **structure of the catalytic species**
3) **Texture** of the catalyst (surface area, pore size, pore volume)
4) **Quality** of the active surface

1) Chemical composition of the bulk and surface of the solids

Elemental composition (bulk) of a catalyst can be determined by spectral methods such as ***AAS (atomic adsorption spectroscopy), ICP-MS (Inductively coupled plasma mass spectrometry), SEM-EDX (*****Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis) analysis, *XRF (x-ray fluorescence)***

XPS (x-ray photoelectron spectroscopy) can be used to determine the surface composition of the catalyst

Determination of Elemental Composition of catalyst

The chemical nature and composition of catalyst surfaces are essential parameters for understanding catalytic reactivity

- **Atomic absorption spectrometry (AAS)** detects elements in either liquid or solid form of the catalyst through the **application of characteristic wavelengths of electromagnetic radiation from a light source**. Individual elements will absorb wavelengths differently, and these absorbances are measured against standards

- **Inductively coupled plasma mass spectrometry (ICP-MS)** is an elemental analysis technique which uses **Inductively Coupled Plasma** (ICP) (plasma formed from Ar gas) **as an ionization source**. This fully **decomposes a sample into its constituent elements** and transforms those elements into ions, which are then detected

- **Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)-** SEM provides detailed **high resolution images of the sample** by using a **focussed electron beam across the surface and detecting secondary or backscattered electron signal**. An Energy Dispersive X-Ray Analyzer (EDX or EDA) is used to provide **elemental identification and quantitative compositional information**.

- **XRF (X-ray fluorescence)** is a analytical technique used to determine the **elemental composition of materials by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source**. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays that is unique for that specific element,

- **X-ray Photoelectron Spectroscopy (XPS)** is a surface analysis technique which provides valuable **quantitative and chemical state information from the surface** of the material being studied

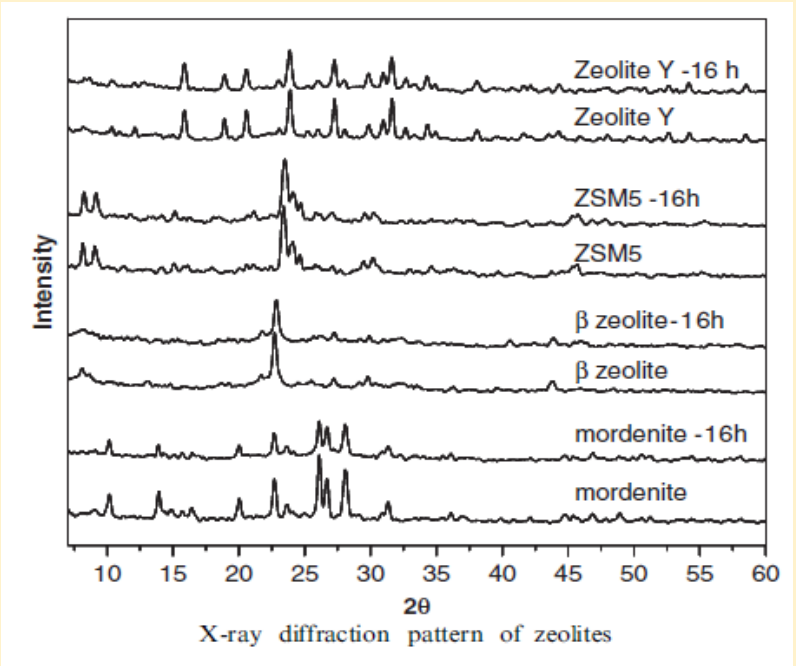
  XPS method **excites a samples surface with mono-energetic Al kα x-rays** causing photoelectrons to be emitted from the sample surface. An electron energy analyzer is used to **measure the energy of the emitted photoelectrons**. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined.

2) Nature and structure of catalysts

- For **crystalline material** – structure and phases can be determined by **XRD (X-ray diffraction) method**
- For **amorphous material** – spectroscopic methods such as **IR (Infra-red) spectroscopy, Raman spectroscopy, UV-Vis (Ultraviolet-Visible) spectroscopy** can be used for identification of molecules by identifying the bonds
- Surface morphology is determined by techniques such as **SEM (Scanning Electron Microscopy)** and **TEM (Transmission Electron Microscopy)**
- **Thermal analysis methods** such **temperature programmed reduction (TPR), temperature programmed desorption (TPD), thermo gravimetric analysis (TGA) and differential thermal analysis (DTA)** are among the techniques used extensively for characterization of catalysts

XRD (X-ray diffraction)

- This is an effective method for determining the structure of crystalline materials (composed of atoms arranged in a regular ordered pattern)
- The crystalline structure causes a beam of incident X-ray to diffract into many different directions
- By measuring the angles and the intensities of these diffracted beams, a 3D picture of the electron densities within the crystal can be produced
- XRD can be used for phase identification and determination of crystallite size



X-ray diffraction pattern of zeolites

Mitra and Kunzru, J Am Ceram Soc, 91(1), 64

Spectroscopic methods

IR spectroscopy

- IR spectroscopy gives information about the molecular structure of materials
- This is a vibrational spectroscopy based on the phenomenon of absorption of infrared radiation by molecular vibrations
- When IR radiation hits a molecule, the bonds absorb the energy and respond by vibrating. Among the total number of normal vibration modes in a molecule, only some can be detected by infrared spectroscopy. To be infrared active, a vibration mode must cause a change of dipole moment in a molecule
- Species with polar bonds, such as CO, NO or OH exhibits strong IR bands.

Raman spectroscopy

- Raman spectroscopy is based on inelastic scattering (scattered light has a different frequency from that of the source radiation) phenomenon of electromagnetic radiation by molecules
- Raman spectroscopy is commonly used to provide a structural fingerprint by which molecules can be identified
- To be Raman active, a vibration mode must cause polarizability changes in a molecule (polarizability is the ease with which an electron cloud is distorted by an electric field)
- Bonds such as symmetric stretching of CO_2 molecule, bonds in the H_2O molecules are Raman active

Ultra-violet-Visible (UV-vis) spectroscopy

- The principle of UV-Visible Spectroscopy is based on the absorption of ultraviolet light or visible light by chemical compounds, which results in the production of distinct spectra
- Absorption of UV radiation by a molecule results in excitation from ground state to high energy state - the more easily excited the electrons, the longer the wavelength of light it can absorb
- Apart from using UV-Visible Spectroscopy for identification and structure determination of compounds, it is also used for the quantitative determination of compounds

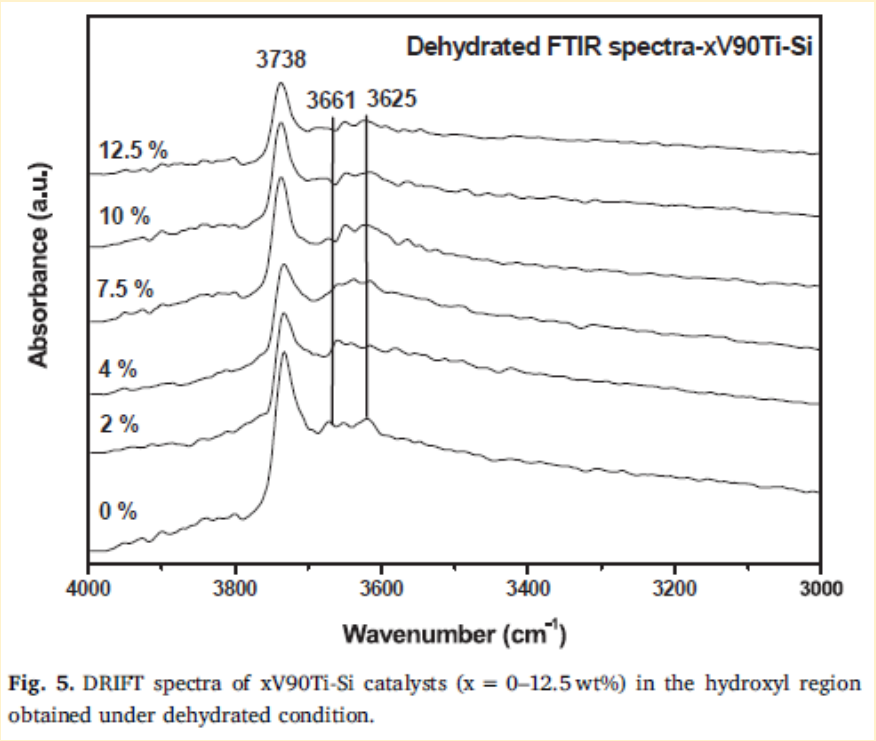


Fig. 5. DRIFT spectra of xV90Ti-Si catalysts (x = 0–12.5 wt%) in the hydroxyl region obtained under dehydrated condition.

IR spectra

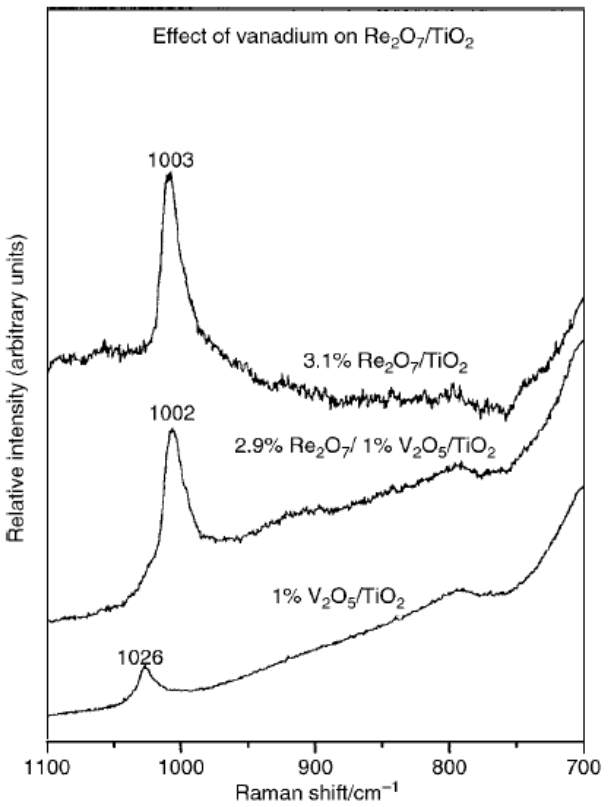


Fig. 3 Raman spectra of vanadium doped Re_2O_7/TiO_2. Spectra obtained under dehydrated conditions.

Raman spectra

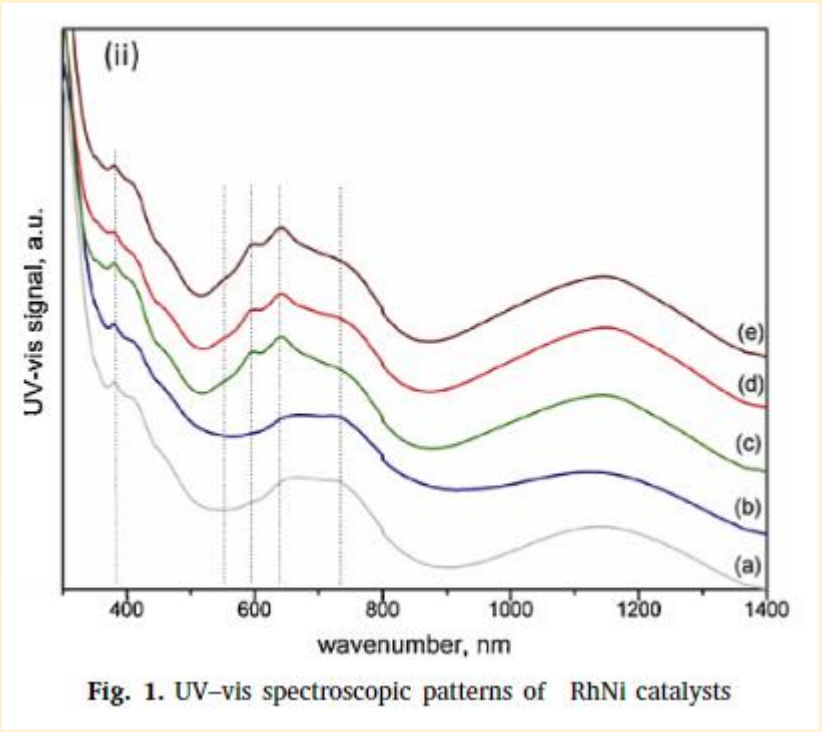


Fig. 1. UV–vis spectroscopic patterns of RhNi catalysts

UV-vis spectra

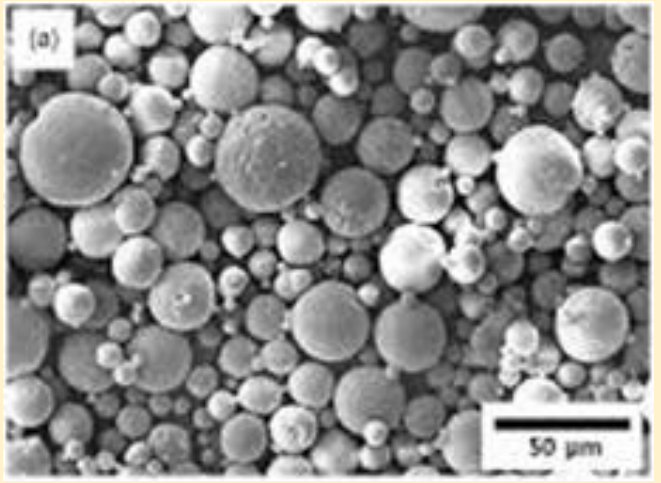
Shee et. Al., Molecular Catalysis, 451, 228

Mitra et. al., Journal of Catalysis, 240, 151

Electron Microscopy

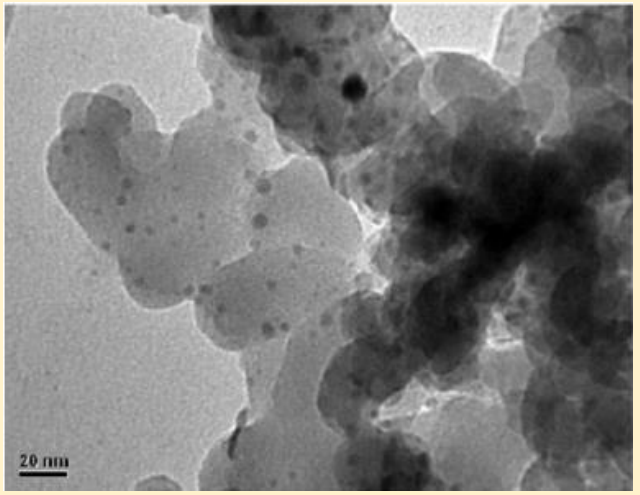
Electron microscopy (EM) is a technique for obtaining high resolution images of specimens using a beam of accelerated electrons as a source of illumination

- **SEM (Scanning Electron Microscopy)** is used to study the microscopic structure of a specimen. SEM produces images by probing the specimen with a focused electron beam that is scanned across the surface area of the specimen



SEM image of spherical Al_2O_3 particles

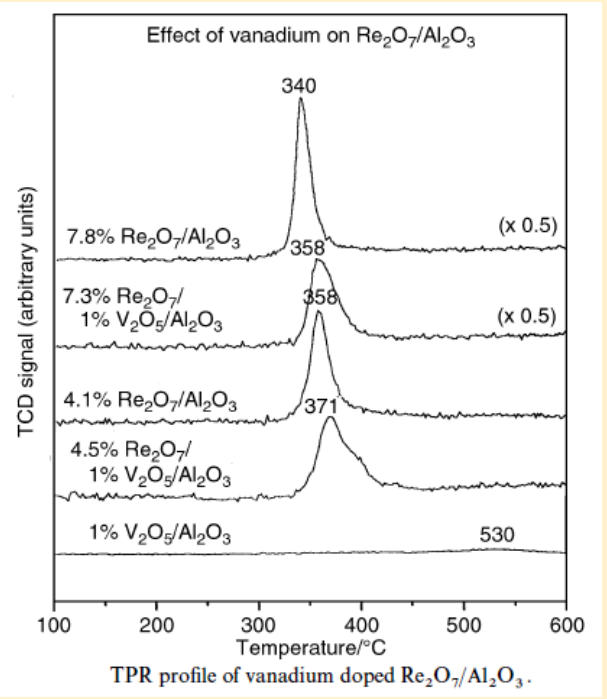
- **TEM (Transmission Electron Microscopy)** gives nano-scale compositional and structural information with images. The transmission electron microscope directs a high voltage electron beam towards the specimen to illuminate it and create a magnified image of the sample. When the electron beam passes through the specimen, it is scattered and provides an image of the microscopic structure of the specimen, which is then recorded



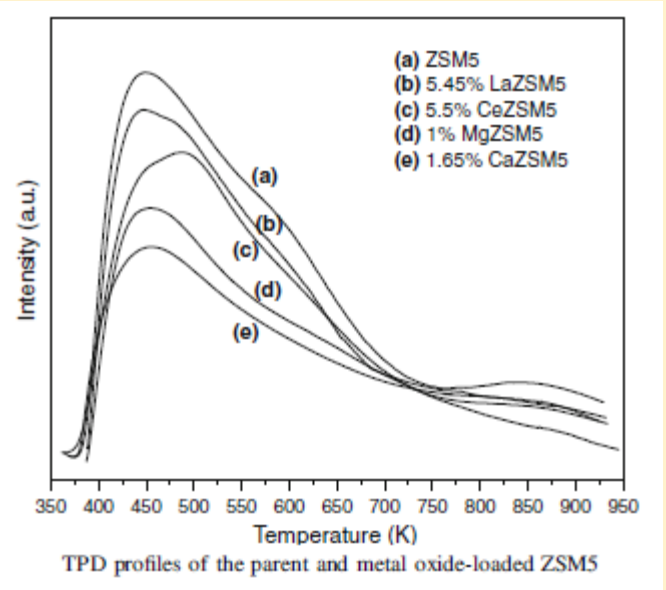
TEM image of Cu nanoparticles on SiO_2

Thermo-analytical techniques

- **Temperature programmed reduction (TPR) -** used to determine the reducibility of the catalysts. Technique involves monitoring the ease of removal of oxygen from the catalytic surface by means of hydrogen while the temperature is increased linearly with time
- **Temperature programmed desorption (TPD)** – used to study the acidic and basic sites on the catalyst surface by measuring the desorbed molecules from the sample surface
- **Thermo gravimetric analysis (TGA)** - used to determine the thermal stability, moisture and volatile material content or decomposition of inorganic and organic material in the catalysts by measuring the change in mass with increase in temperature at specified gas environment and heating rate
- **Differential thermal analysis (DTA)** – involves heating a sample and reference material at the same rate and monitoring the temperature difference between the sample and reference. useful to detect phase changes associated with calcination process



TPR profile of vanadium doped Re_2O_7/Al_2O_3.



TPD profiles of the parent and metal oxide-loaded ZSM5

Mitra et. al., Physical Chemistry Chemical Physics, 3, 1144
Mitra and Kunzru, Chemical Eng and Proc: Process Intensification, 64, 48