

CHAPTER 1

INTRODUCTION

1.1 Background

The investigation of chemical reactions by *in situ* and operando diffuse reflectance FT-IR spectroscopy (DRIFTS) can bring many invaluable insights into the mechanism of heterogeneous catalytic reactions [1-6]. Recent work by Centre for the Theory and Application of Catalysis (CenTACat) laboratory has re-emphasized that chemical steady-state conditions must be maintained to investigate the true reactivity of surface species under reaction conditions [2, 7-9], stressing the advantages of using chemical-steady-state isotopic transient techniques to investigate the true reactivity of adsorbates. A DRIFTS reactor is particularly suitable to this type of spectrokinetic investigation since the catalyst powder can be used directly as such, whereas transmission techniques require pressing wafers, which can lead to mass-transport limitations and catalyst modifications. DRIFTS spectroscopy possesses a number of other advantages over transmission FTIR, and is becoming the most widespread FTIR technique for catalytic applications at the gas-solid interface. DRIFTS exhibits a higher sensitivity with respect to surface species and strongly absorbing samples such as carbon-based materials can be studied [10-18]. This increasing popularity is also due to the availability of a number of affordable commercial cells, while a few research groups have built custom-made cells [19].

The qualitative analysis of the DRIFTS spectra is sufficient to assess the nature of the adsorbates present. However, a fully quantitative analysis of DRIFTS data is required when the surface concentrations and the specific rate constants of

reaction (or desorption) of adsorbates are needed to carry out to complete the spectrokinetic studies. Ideally, a function of the DRIFTS intensity that is linear with the adsorbate surface concentration would be preferred. Griffiths et al. [12-13] and several other groups [10, 15, 20-21] discussed the quantification of DRIFTS analyses, and observed that the domains of linear response between solute/sorbate concentration and DRIFTS intensity transformation were somewhat narrow.

It is surprising that the nature of the DRIFTS intensity function to be used to represent the surface concentration of adsorbates seems yet rather unclear. A brief survey in numerous papers dealing with DRIFTS studies of adsorbates published (particularly in heterogeneous catalysis journals) over the 2005-2006 period revealed that the Kubelka-Munk function was appeared in about half of the papers, while the absorbance ($= \text{Log } 1/R$) function was recommended in another half. The basis of the selection of function was not discussed. The lack of clarity as to which intensity transformation to be used is partly due to the fact that there is no direct mean of measuring the surface concentration of an adsorbate and the corresponding DRIFTS signal intensity. Note that this is no longer the case for transmission FTIR, for which a combined gravimetric microbalance-IR cell has been built [22-23].

The first part of this work discussed the basis of DRIFTS quantitative analysis for both “solute in a solid” and “adsorbate on a solid” systems, the latter case being the one most relevant to heterogeneous catalysis. Both theoretical and experimental considerations were presented to assess the most appropriate mathematic transformation to be used to relate adsorbate surface concentration and DRIFTS signals. The experimental data were based in part on the adsorption of CO on Pt/SiO₂. Some absorbance spectra already reported elsewhere [24-25] which related

to the reactivity of formate species over Pt/CeO₂ were re-evaluated and allow to compare with other intensity transformations.

1.2 Infrared Spectroscopy [26-28]

Infrared (IR) spectroscopy can be considered as the first important modern spectroscopic technique that has found general acceptance in catalysis. The most common application of IR in catalysis is to identify the adsorbed species and to understand the way in which these species are chemisorbed on the surface of the catalyst. In addition, the technique is useful in identifying phases that are present in precursor stages of the catalyst during its preparation. Sometimes the infrared spectra of adsorbed probe molecules such as CO and NO give valuable information on the adsorption sites that are present on a catalyst.

Vibrations in molecules or in solid lattices are excited by the absorption of photons (IR spectroscopy), or by the scattering of photons (Raman spectroscopy), electrons (electron energy loss spectroscopy) or neutrons (inelastic neutron scattering). If the vibration is excited by the interaction of the bond with a wave field, as with photons and electrons, the excitation is subject to a strict selection rules.

Collisions, on the other hand, excite all vibrational modes.

Infrared spectroscopy is the most common form of vibrational spectroscopy. Infrared radiation falls into three categories, as indicated in Table 1.1. It is the mid-infrared region that is of interest.

Table 1.1 Classification of infrared radiation

Region	Wavelength (μm)	Energy (meV) ^a	Frequency (cm^{-1})	Detection of
Far	1000-50	1.2-25	10-200	Lattice Vibrations
Mid	50-2.5	25-496	200-4000	Molecular Vibrations
Near	2.5-1	496-1240	4000-10000	Overtone

Note a: $1 \text{ meV} = 8.0655 \text{ cm}^{-1}$

Infrared spectroscopy is a typical of *in situ* methods for catalyst characterisation. It was probably the first form of spectroscopy applied to catalyst characterisation and continues to be the most widely used spectroscopic tool for study of catalyst and surfaces chemistry. Infrared spectroscopy provides information on the nature of adsorption, acid and active sites present on catalyst surfaces during preparation and reaction. Using special flow cells, it is possible to collect *in situ* reaction spectra at reaction temperatures up to 500 °C and pressures of 1-2 atm on supported catalysts. The kinds of information available from IR regarding the structure and coverage of adsorbates and the nature of catalytic surfaces during adsorption and *in situ* reaction are summarized, the structure of adsorbed reactants, products and reaction intermediates, such as stoichiometry, charge, geometry and coverage; the nature of catalytic surface, such as oxidation state, acidity, index plane and site molecularity (number of atoms).

Vibration in IR is excited by absorption of photons. Infrared radiation generally in the range of $4000\text{--}400\text{ cm}^{-1}$ is used to excite molecular vibrations of four types as: stretching, bending in one plane, bending out of plane, and torsional. In general, the stretching vibrations are of the highest frequency and the most relevant to catalyst studies. Since absorption of an IR photon occurs only if a dipole moment changes during vibration, species with polar bonds such as CO, NO and OH exhibit strong IR bands, whereas covalent bonds such as C-C, N=N, H_2 and N_2 absorb IR are either weakly or not at all.

The characteristic IR bands can be divided into five regions [27] as follows:

- The X-H stretch region ($4000\text{--}2500\text{ cm}^{-1}$), e.g. strong bands for OH, NH, CH and SH stretch vibrations are observed
- The triple bond region ($2500\text{--}2000\text{ cm}^{-1}$), e.g. gas phase CO (2143 cm^{-1}) and linearly adsorbed CO ($2200\text{--}2000\text{ cm}^{-1}$)
- The double bond region ($2000\text{--}1500\text{ cm}^{-1}$), where in catalytic studies bridge-bonded CO, as well as carbonyl groups in adsorbed molecules (around 1700 cm^{-1}) absorb
- The fingerprint region ($1500\text{--}500\text{ cm}^{-1}$), where all single bonds between carbon and elements such as nitrogen, oxygen, sulphur and halogens absorb
- The metal-adsorbate region ($450\text{--}200\text{ cm}^{-1}$), where the metal-carbon, metal-oxygen and metal-nitrogen stretch frequencies in the spectra of adsorbed species are observed

Experimentally, several forms of IR spectroscopy are in use, as illustrated in Figure 1.1. The common forms of the techniques are (1) transmission IR or FTIR

through a thin wafer to the detector, (2) diffuse reflectance IR spectroscopy (DRIFTS) involving reflectance of IR radiation from a powder to an ellipsoidal mirror which collects and focuses it on the detector and (3) reflectance IR from a flat metal surface. The source is generally a temperature-stabilized ceramic filament operating around 1500 K, while the standard detector is deuterium triglycine sulphate. Most transmission IR instruments these days are Fourier-transform infrared (FTIR) spectrometers which operate on the principle of the Michelson interferometer, i.e. the entire spectrum is obtained for each scan of the interferometer, enabling rapid collection. Commercial IR cells are now available which enable operation for the transmission mode above 500 °C and for DRIFTS up to 900-1000 °C; cell windows can be made of NaCl, KBr and CsI with lower frequency cut offs at 650, 400 and 200 cm^{-1} , respectively.

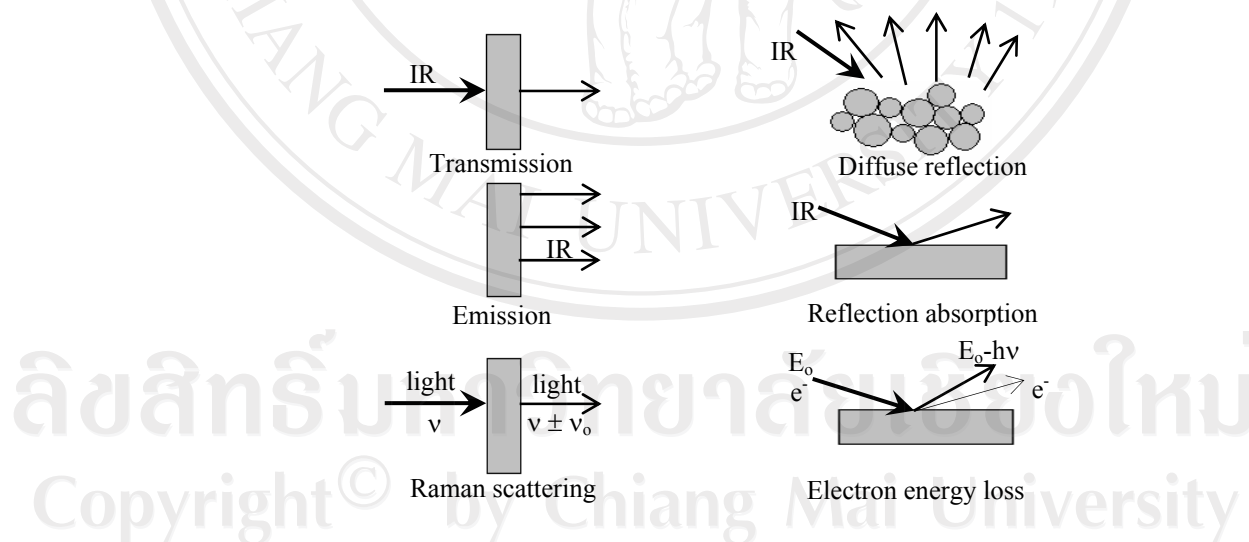


Figure 1.1 Six different ways to perform vibrational spectroscopy (adapted from [26])

1.3 Diffuse Reflectance Infrared Fourier Transform Spectroscopy [29-31]

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique that collects and analyzes scattered IR energy. It is used for measurement of fine particles and powders, as well as rough surface sample (e.g., the interaction of a surfactant with the inner particle, the adsorption of molecules on the particle surface). Sampling is fast and easy because very little or no sample preparation is required. Information about the molecules adsorbed on the surface of a catalyst is given.

Any radiation focused on a surface can, depending on the characteristics of the surface and its environment, be absorbed, directly reflected (specular reflection), internally reflected, or diffused in all directions. The latter effect is of interest in diffuse reflection spectroscopy. One of the principal advantages of this technique is the ability to obtain infrared spectra of solid materials without cumbersome sample preparation. However, DRIFTS spectra may be extremely difficult to interpret because they closely depend on the conditions in which they are obtained. As shown in Figure 1.2, infrared radiation may be directly reflected by the sample surface, giving rise to specular reflection, which is a function of the refractive index and absorptivity of the sample. The radiation may also undergo multiple reflections occurring at the surface of the particles and without penetrating the sample.

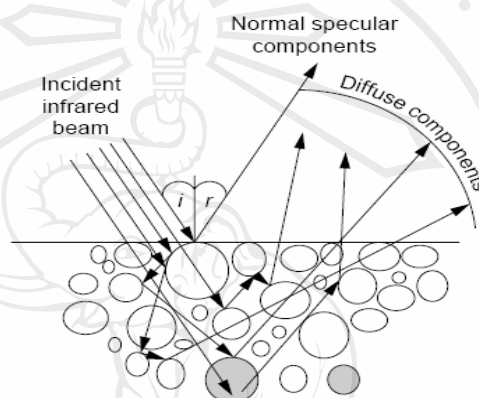
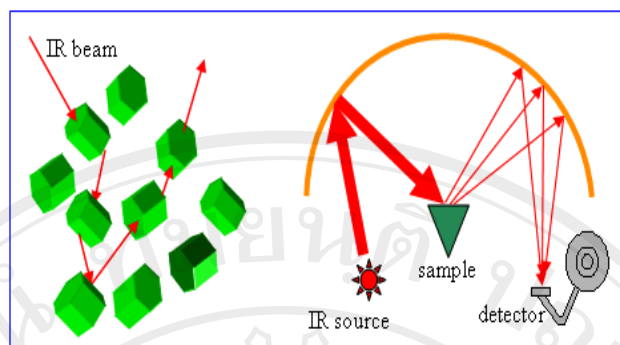


Figure 1.2 Mechanisms generating the infrared spectrum of a powder [30-31]

The radiation that undergoes this type of diffuse specular reflection exits the surface at any given angle relative to that of the incident beam. On the contrary, true diffuse reflection is the consequence of beam penetration into one or more particles and its diffusion in the sample. This component of the radiation also exits the sample at any angle but, since it has traveled through the particles, it contains data on the absorption properties of the material. In consequence, this complex radiation contains similar data to those of a transmission spectrum, and this is why it is advantageous from the IR standpoint. However, diffuse reflection cannot be optically separated from specular reflection, but if the specular diffuse reflection component is weak compared with diffuse reflection (absorptivity of the material not too high), diffuse

reflection spectra are very similar to transmission spectra. The contribution of specular reflection to the total signal is the main cause of the distortion of DRIFTS spectra.

There are three ways to prepare samples for DRIFTS measurement:

1. Fill the micro-cup with the powder (or the mixture of the powder and KBr). The diffuse reflectance accessory uses a focusing mirror to focus the beam on the sample surface and collect the IR energy. The micro-cup needs to be filled consistently in order to keep the focus.
2. Scratch the sample surface with a piece of abrasive (SiC) paper and then measuring the particles adhering to the paper.
3. Place drops of solution on a substrate. If colloids or powders are dissolved or suspended in a volatile solvent, a few drops of the solution can be replaced on a substrate, and then evaporate the solvent, subsequently analyze the remaining particles on the substrate.

It is well known that particle size is a key variable in a transmission measurement with the pellet method. Large particle will result in the scattering of the energy, leading to the shift of the spectrum baseline and the broadening of IR bands. The scenario becomes worse in a diffuse reflectance measurement, because the infrared light travels in the sample for a long period and the optics collects a large portion of the distorted energy. It is important to grind the sample particles to 5 microns or less.

As a rule, the specific properties of the material liable to influencing the quality of the DRIFTS spectrum are as follows: refractive index of the sample,

particle dimensions, packing density, homogeneity, concentration and absorption coefficients.

In the case of inorganic or strongly absorbent materials, the first three properties can cause significant distortions in the form and relative intensity of the bands, to the extent of having negative bands. To decrease the contribution due to external reflection of the largest particles, the sample can be ground into smaller particles. A size smaller than $10\text{ }\mu\text{m}$ (*i.e.* not exceeding the wavelength of the incident radiation) is preferable. If the sample is high absorbing material, it must be diluted in a nonabsorbent matrix (potassium chloride, KCl or potassium bromide, KBr). In general, dilution guarantees deeper penetration of the incident ray and less specular reflection of the sample surface, thereby increasing the contribution to the spectrum of components which contain data on the absorbance properties. In certain cases, however, as for zeolites, this type of matrix cannot be used because of interactions with the sample. If so, the use of pure zeolite powder is indispensable. From the theoretical standpoint, there is no linear relation between band intensity and concentration, and quantitative analyses by the DRIFTS method are rather complicated.

The Lambert-Beer law, normally used in transmission, is not directly applicable. However, a similar expression can be found by applying the Kubelka-Munk equation. In a given sample, of thickness d , subject to an incident flux I_0 in direction x and which reflects a flux J_0 along the same axis but in the opposite direction (Figure 1.3). In the element of thickness dx , the fraction of light transmitted is proportional to k (absorption coefficient) and the fraction of light diffused is proportional to parameter s (diffusion factor).

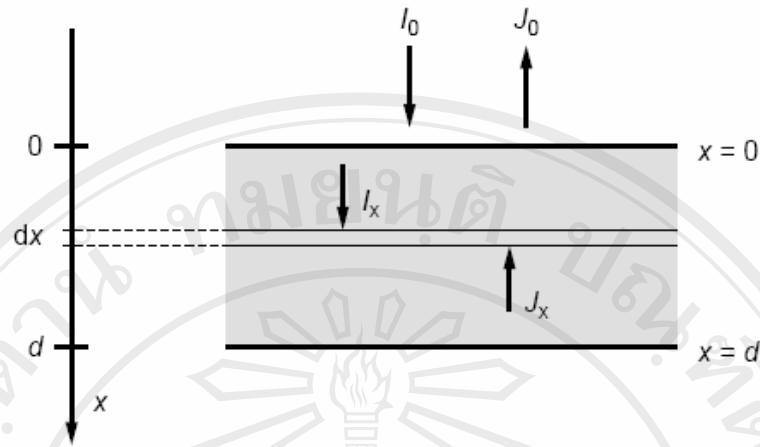


Figure 1.3 Schematic representation of a layer of particles which absorb and diffuse light [30]

Using this simple model, we can show that the transmittance (ratio of the intensity of the exiting light to the entering light crossing the sample) can be expressed by:

$$T = \frac{I_{x=d}}{I_0} = \frac{2\beta}{(1 + \beta^2) \sinh(k'd) + 2\beta \cosh(k'd)} \quad (1.1)$$

and diffuse reflection:

$$T = \frac{J_{x=0}}{I_0} = \frac{(1 - \beta^2) \sinh(k'd)}{(1 + \beta^2) \sinh(k'd) + 2\beta \cosh(k'd)} \quad (1.2)$$

in these expressions:

$$k' = |k(k + 2s)|^{1/2} \quad (1.3)$$

$$\beta = \left| \frac{k}{h + 2s} \right|^{1/2} \quad (1.4)$$

While k , the absorption coefficient, is easily known from the Lambert-Beer law, parameter s is difficult to determine. To circumvent this problem, Kubelka and Munk considered the limiting case of a sample of infinite thickness (2 or 3 mm of powder satisfies this condition). This accordingly gives:

$$T_{\infty} = 0 \text{ and } R_{\infty} = (1 - \beta) / (1 + \beta) \quad (1.5)$$

which can also be placed in the form:

$$\frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} = f(R_{\infty}) \quad (1.6)$$

$f(R_{\infty})$ is called the re-emission function or Kubelka-Munk function. A comparison with a standard sample consisting of a very nonabsorbent powder, *i.e.* KCl, KBr, etc. (such that $k \cong 0$ and $R_{\infty} \cong 1$) helps to determine the ratio:

$$r_{\infty} = (R_{\infty})_{\text{sample}} / (R_{\infty})_{\text{standard}} \quad (1.7)$$

which apply to the expression:

$$f(r_{\infty}) = (1 - R_{\infty})^2 / 2 R_{\infty} = k/s \quad (1.8)$$

by replacing k by $2.303 \cdot \epsilon \cdot c$, where:

ϵ = extinction coefficient (function of the wavenumber ν); c = sample concentration; this gives:

$$f(r_{\infty}) = 2.303 \cdot \epsilon(\nu) \cdot c/s \quad (1.9)$$

and if s is a constant, *i.e.* an intrinsic property of the material which depends on the grain size, $f(r_{\infty})$, at a given frequency, varies directly with the sample concentration, c . This produces a similar expression to the absorbance expression that enables to obtain a spectrum resembling the transmission spectrum.

Diffuse reflection measurement are mostly limited to a semi-quantitative analyses. This technique is extremely useful for examining samples that are difficult to analyze in transmission spectroscopy method.

1.3.1 DRIFTS Apparatus

Figure 1.4 shows the apparatus for the DRIFTS measurement. The infrared beam is focused by a series of mirrors on the surface of the sample, which is placed in a sample holder. Diffuse radiation through the powder is collected by other mirrors and sent to the detector.

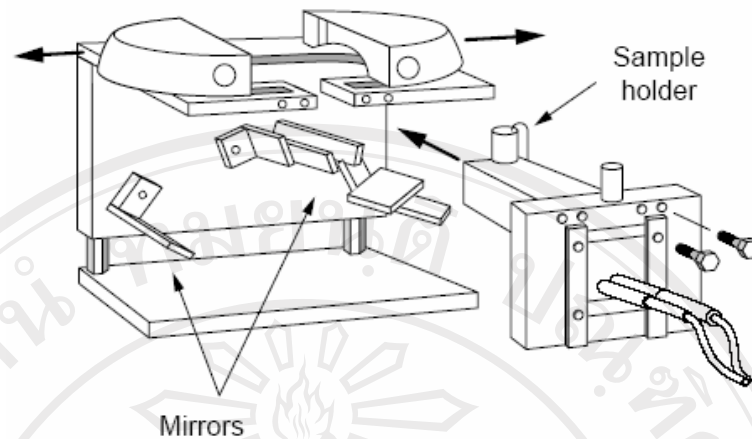


Figure 1.4 Apparatus for diffuse reflection measurement [31]

The apparatus can be equipped with an *in situ* high temperature and high pressure cell as shown in Figure 1.5.

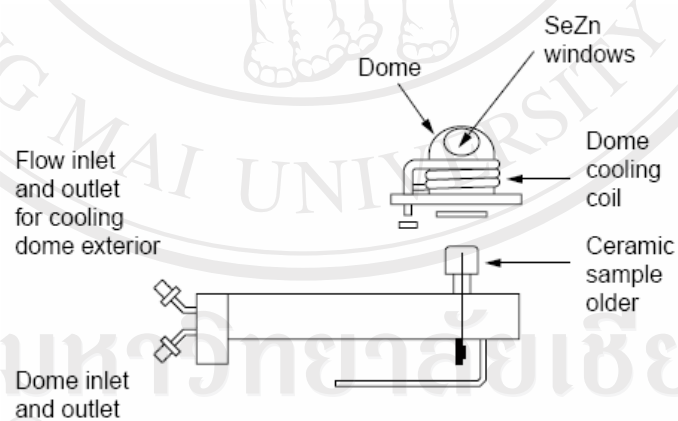


Figure 1.5 Sample holder and dome [31]

The sample holder, a ceramic crucible containing a heating resistor and a thermocouple, is placed inside a dome with zinc selenium (SeZn) windows. To

remove the heat, the dome is surrounded by coils conveying a stream of nitrogen gas kept at low temperature by a heat exchanger immersed in liquid nitrogen. To prevent condensation on the windows, the liquid nitrogen flow rate must be regulated as a function of the final sample temperature. An inlet and outlet are provided to send the gases into the dome and through the sample.

Figure 1.6 shows the path of the gases inside the dome. The gases pass through the sample from the bottom upward. This flow direction offers the advantage of thermostatically controlling the gases and tracking the surface reactions at the desired temperatures.

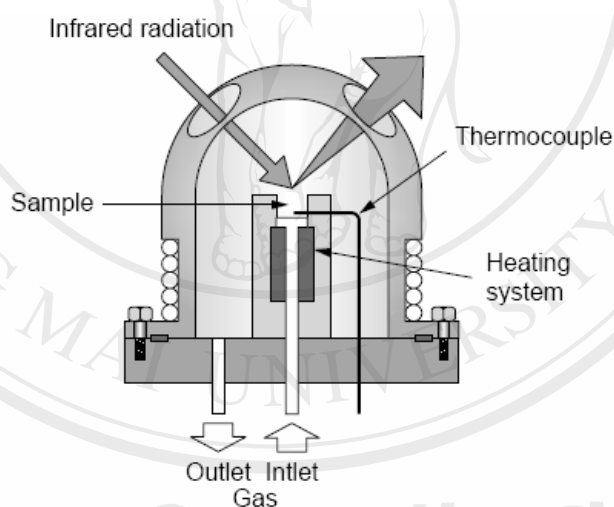


Figure 1.6 Dome interior [31]

1.3.2 Characteristics of DRIFTS technique: advantages and drawbacks

The DRIFTS technique offers the advantages of simpler sample preparation, the capacity to analyze nontransparent samples, irregular surfaces and coatings (polymer, etc.), exposure of the sample to simulated reaction conditions while analyzing the changes in the species at the material surface, recording of the spectrum of the powder at elevated temperature and/or under pressure. The main drawback is the difficulty of quantitative measurement. Another limitation concerns the repetitivity of the measurement setting. Since the diffusion coefficient varies with each preparation, it is difficult to compare two spectra of the same material recorded in two different experiments. To overcome this problem, the spectra can be brought to iso-intensity of a structure band. Other drawbacks concern the implementation of the diffuse reflection experiment to analyze catalysts. A high temperature gradient exists between the upper edge and bottom of the crucible containing the sample. The infrared radiation cannot see the entire thickness of the catalytic bed but only the sample surface. In consequence, differences may be recorded between the reactivity observed by the changes in the bands of the species at the surface and that obtained by analyzing the gases exiting the cell.

1.4 Heterogeneous Catalysis [27, 32-33]

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst and leave it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cycle event in which the catalyst participates and is recovered in its original form at the end of the cycle.

The catalysis between molecules A and B gives a product P, as shown in Figure 1.7. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, when is also bound to the catalyst. In final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.

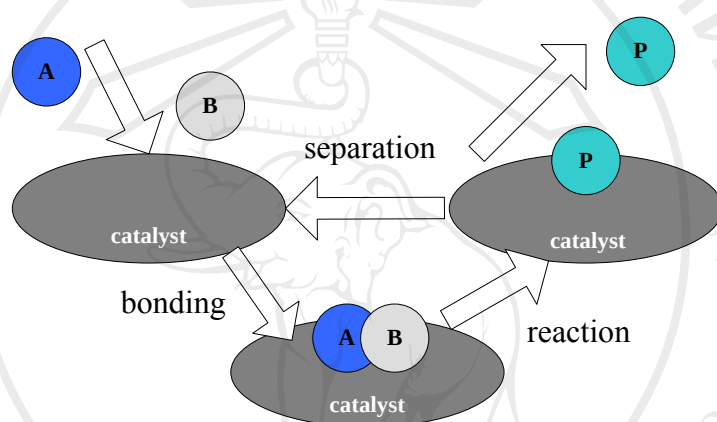


Figure 1.7 A sequence elementary steps of the catalytic reaction (adapted from [33]).

Heterogeneous catalyzed reactions are composed of purely chemical and purely physical reaction steps. For the catalytic process to take place, the starting materials must be transported to the catalyst. Thus, apart from the actual chemical reaction, diffusion, adsorption, and desorption processes are of importance for the progress of the overall reaction.

Heterogeneous catalysts may consist of metals, metal oxides, metal salts, or mono-metal oxides. Very often the active catalyst is supported by another material. The supports may be silica, alumina, active carbon, etc. Its function is threefold; it

dilutes the active catalyst and makes it more accessible to the reactants. The support reduces the amount of active component which is required to achieve a certain activity. This is obviously an advantage when expensive compounds or noble metals are used as active catalysts.

The support can enhance the mechanical stability of a catalyst and participate in the reaction by activating the reactant or by favoring certain reaction pathways over others.

Catalysts can be made in many different macroscopic forms. They can be applied as a powder, a sand-like granulate, tablets or pellets. Automobile exhaust gas or flue gas denitrification catalysts are usually monoliths. These are porous blocks with channels parallel to the gas flow. They allow very high flow rates, since they cause a small pressure drop along the catalyst. A skeleton catalyst consists of a metal skeleton, obtained by dissolving one component of an alloy with acid or base leaving the more noble metal component.

Heterogeneous catalysts are chiefly produced by one of the four general processes; mixing, impregnation, precipitation, or metal alloy treatment by partial corrosion.

In heterogeneous catalysis chemisorptions of the reactant and products on the catalyst surface is of central importance, so that the actual chemical reaction on the catalyst surface can not be considered independently from adsorption of the reactants on the inner surface of the pores and desorption of the products from the catalyst surface. Therefore, these steps must be included in the microkinetics of the reaction.

1.4.1 Catalyst materials

A typical heterogeneous catalyst comprises of three components: an active catalyst phase, a high surface area carrier (support) which serves to facilitate the dispersion and stability of the active catalytic phase, and a promoter which increases activity and/or stability.

1.4.1.1 Active catalytic phase

Transition metals and/or their oxides, sulfides, carbides and nitrides are unique in their abilities to catalyze chemical reactions, primarily due to their multiplicity of low energy surface electronic states which can readily donate or accept electrons in the processes of making or breaking bonds at a surface.

1.4.1.2 Carrier

Catalyst carriers (supports) are porous, high-surface-area metal oxides or carbons having significant pore volume and capacity for preparing and preserving during stable reaction, well-dispersed catalytic phases. Surface area of these materials range from about 1.5 to 1500 m²g⁻¹, pore volumes are generally 0.4-1 cm³g⁻¹, and pore diameters range from 0.4 to 2000 nm.

1.4.1.3 Promoters

Promoters are of two kinds, textural and chemical. Textural promoters are generally employed to facilitate the preparation of a well-dispersed catalytic phase and maintain their well-dispersed state during reaction condition. Textural promoters include supports discussed in the previous section as well as additives such as

alumina, silica or other relatively inert, high surface oxides that serve the above two purposes. Chemical promoters are additives that enhance the activity or selectivity of the catalytic phase. Typical chemical promoters include alkali and alkaline earth metals or metal oxides.

1.4.2 Catalyst preparation

A general scheme for preparation of supported catalysts and their forming is shown in Figure 1.8.

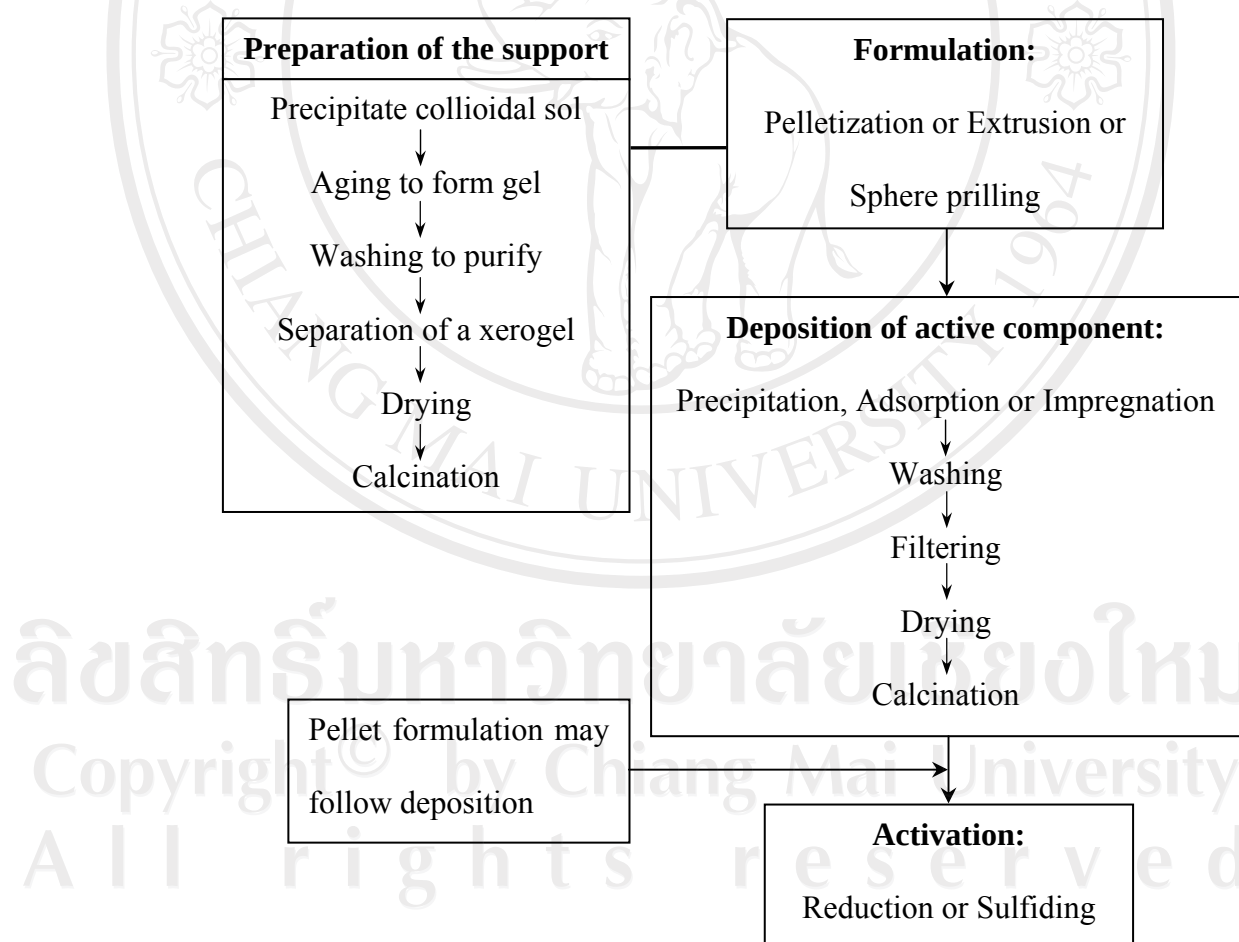


Figure 1.8 A general scheme illustrating typical routes for catalyst preparation (adapted from [27])

1.4.2.1 Deposition of the active component onto a support by impregnation

The simplest and probably the most common procedure for dispersing a catalyst species on a carrier homogeneously is by impregnating the pre-dried support to incipient wetness with an aqueous or non-aqueous solution containing a salt (precursor) of the catalytic element or elements. The precursor salt is dissolved in a volume of solvent equal to the catalyst pore volume, and this solution is added slowly (sometimes dropwise) to the support in which capillary forces of up to several hundred atmospheres draw the liquid into the pores. Addition of solution continues until the pores of the support are saturated as evident by the beading of the excess solvent. The precise amount of catalytic species is assured to be present in the carrier. This procedure is illustrated in Figure 1.9(a). Upon drying in either air, inert gas or vacuum (typically at 80-150 °C) crystallites of the precursor are deposited inside the pores. The rate of drying, as determined by temperature and flow rate of the gas, affects the deposition of the active material in the pores as illustrated in Figure 1.9(b). At low rates of drying, evaporation occurs at the meniscus which retreats down to the pore. Most of the precursor is deposited at the deepest end of the pore in the pellet center. If drying step is too fast (this generally occurs at high drying temperatures), a temperature gradient is set up and vaporization occurs deep in the pores and forces the precursor deposit to the pore entrances and leading to an eggshell deposit in the pellet. Since pores of any typical carrier are distributed over a wide range of sizes, it is difficult to optimize the rate of drying so that uniform deposition occurs in all the pores. Of course, it is sometimes desirable, for example in the case of reactions controlled by film mass transfer, to deposit the catalyst in a thin sheet at the outer

shell or in the case of pore mouth poisoning to deposit the active phase enters the interior of the pellet.

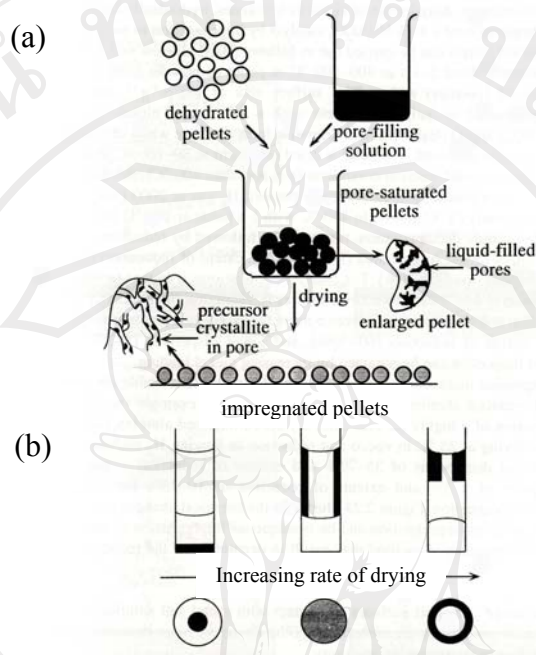


Figure 1.9 Schematic of steps in the preparation of supported catalysts by (a) impregnation to incipient wetness (b) pore and particle profiles after drying at different rates [27]

The advantages of the impregnation method include its relative simplicity, rapidity and capability for depositing the precursor at high metal loadings. A principle disadvantage is that sometimes material is non-uniformly deposited along pores and through the pellet. Another is the tendency for deposited base metal precursors to be oxidized in the aqueous solution to oxides that interact strongly with alumina or silica supports and which are difficult to reduce.

1.4.2.2 Precipitation

The method is to precipitate the catalyst precursor in the form of a hydroxide or carbonate in the pores and on the surface of the carrier by adjusting the pH of the metal salt solution-support slurry through addition of a base such as NaOH, NH_4OH or Na_2CO_3 . Alternatively, support and catalyst precursor are coprecipitated together, such as the coprecipitation of Ni hydroxide on silica by pouring together the aqueous solutions of sodium silicate and nickel nitrate. Base and metal salt are carefully chosen to avoid the presence of species in the final catalyst that might later act as poisons, such as Na^+ and SO_4^{2-} for hydrogenation processes.

The overall sequence of procedures in supported catalyst preparation by precipitation is illustrated in Figure 1.10. Generally, support in the form of pellets or powder is added to the salt solution, after which the alkali solution is usually added dropwise accompanied by rapid stirring of the slurry. Upon addition of sufficient alkali solution, catalyst precursor sols precipitate in the pores and/or catalyst precursors are formed by reaction at the interior surfaces of the support.

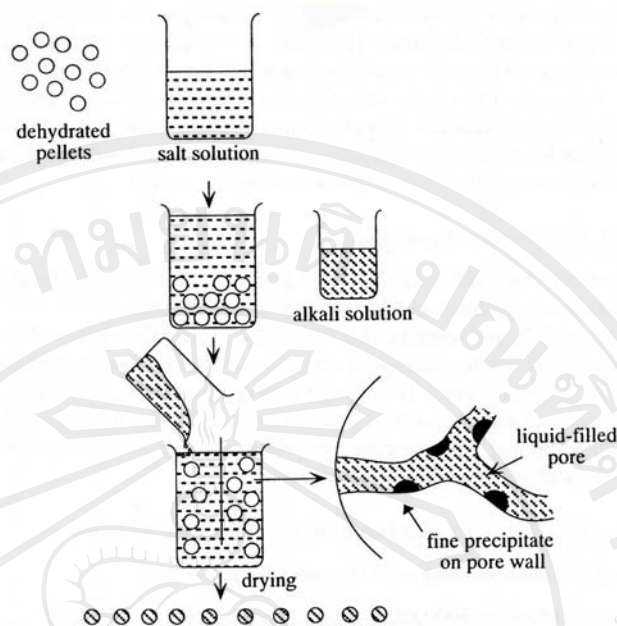


Figure 1.10 Schematic of steps in the preparation of supported catalysts by precipitation from alkali solution [27]

1.4.3 Catalyst activation

1.4.3.1 Calcination

The high temperature in air is often the last step in producing oxide catalysts or next to the last step in producing metal or metal sulfide catalysts. Its purpose is to decompose and volatilize various catalyst precursors and no longer in which formed in preparation, such as hydroxides, nitrates or carbonates the desired forms for the final catalyst. For decomposition of unsupported hydroxide or carbonate precursors, or precursors supported on inorganic oxide carriers, calcination is typically conducted in air at temperatures of 300-500 °C. Great care must be taken to carefully pre-dry the solid and to avoid rapid heat-up during calcination since H₂O trapped inside the micropores can build up sufficient pressure to crack the particulate

carriers. Furthermore, exothermic reactions due to decomposing salts can cause localized high temperatures within the catalyst material resulting in acceleration of sintering the carrier and the catalytic material.

1.4.3.2 Reduction

This treatment is the final step in the production of unsupported and supported metal catalysts, the purpose is to convert oxides and/or catalyst precursor salts to metal by treatment in hydrogen or other reducing agents such as CO, synthesis gas (CO and H₂) and hydrazine. Regarding to the reduction process, the following principles and empirical observations which based on published literatures are emphasized:

(a) The reducing agent should be carefully purified eliminate off impurities such as oxygen, sulfur, water and hydrocarbons which serve to contaminate the catalyst, or in the case of water and oxygen, reverse the reduction process.

(b) Temperature, the most important variable in the reduction process, needs to be carefully optimized for each supported metal system.

(c) Heating rate and hydrogen space velocity are important variables in the reduction that also require careful optimization. Generally, lower heating rates (5-10 °C min⁻¹) and high H₂ space velocities (2000-3000 h⁻¹) favor production of catalysts of high metal-surface-area and extent of reduction, since these conditions enable fast removal of reactive water and thereby reduce the partial pressure of water in the catalyst which would otherwise inhibit reduction and facilitate metal species transport and sintering.

(d) The important of sensitivity in catalyst properties, such as surface area and activity should be optimized. The highly dispersed metals are often pyrophoric when exposed to air, it is essential that prereduced catalysts be carefully passivated before shipping or transferring in open air. Passivation involves purging the sample to remove hydrogen (preferably at the reduction temperature) followed by exposure at 25 °C to a low concentration of oxygen or air (less than 1%); this mild oxidation protects the catalyst by forming an inert oxide layer, a few atoms depth on the outside of each metal crystallite.

1.4.3.3 Sulfiding

This treatment is the final step in the production of sulfide catalysts, typically involves exposing the catalyst to an $\text{H}_2\text{S}/\text{H}_2$ mixture at high temperature to convert oxides or other catalyst precursors to metal sulfides.

1.5 Chemisorption [27, 34-35]

Chemisorption is the bonding of atoms or molecules to a solid surface.

Chemisorption refers to bonds of ‘chemical strength’ as opposed to physisorption which refers to weaker bonds that can only be stabilised on the surface at low temperatures. Because chemisorption involves energies that are sizable on a chemical scale the chemisorption process is often associated with the breaking of bonds. The adsorbing molecules may dissociate during the process, but it has also become clear over the last few years that violent things can happen to the surface itself so bonds between surface atoms may break up and the surface then takes on a completely new structure.

Chemisorption is a method for measuring dispersion. The most active, selective catalysts are typically materials that are either amorphous or that contain extremely small crystallites which for all practical purposes are X-ray amorphous. Chemisorption measurement can be used to estimate the number of active sites for a specific catalyst in a specific reaction thus enabling the determination of turnover frequency (TOF) and as means of quality control, such as determining the change in available metal surface area resulting from different preparation procedures and/or process conditions such as high temperature exposure which may lead to sintering and thus deactivation of the catalyst. Chemisorption measurement is also valuable in obtaining basic information about catalytic reactivity as a function of metal structure and support, such as structure sensitivity and metal-support effects.

1.5.1 Chemisorption of gases on metals

Metal surface chemisorbed gases so readily and often so tenaciously that obtaining perfectly clean surface, free from previously chemisorbed gases was a serious experimental problem in the study of chemisorption of gases by metals. The usual source of surface contamination in the ambient atmosphere from which oxygen is readily chemisorbed even at room temperature and not eliminated by normal evacuation procedures, since the dissociation pressures in most of the metal oxides are much lower. Much of the earlier work on the chemisorption of gases by metals is vitiated by surface contamination because a monatomic layer of oxygen or nitrogen is all that is required to drastically alter the electronic character of the surface from that of metal to that of a semiconductor.

The bases of chemisorption studies on metal surfaces are prepared in the form of evaporated films of pure metals. Trapnell [35] has studied the chemisorption of gases on a variety of metals and data obtained are given in Table 1.2, which shows that metals are divided into seven groups according to the number of gases adsorbed at room temperature.

Table 1.2 Chemisorption of gases by metals [35]

Group	Metals and periodic classification							Gases chemisorbed						
	IIA	IVA	VA	VIA	VIII-1	VIII-2	VIII-3	O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
A	Ca	Ti	V	Cr	Fe									
		Zr	Nb	Mo	Ru									
	Ba	Hf	Ta	W	Os			+	+	+	+	+	+	+
B ₁						Co	Ni	+	+	+	+	+	+	+
B ₂						Rh	Pd							
						Ir	Pt	+	+	+	+	+	-	-
C	Al	Mn	Cu					+	+	+	+	-	-	-
D	K							+	+	-	-	-	-	-
E	Mg	Ag	Zn	Cd	In	Pb		+	-	-	-	-	-	-
F	Au							-	-	-	-	-	-	-

Note: + chemisorbed; - not chemisorbed

For each metal, the strength of adsorption decreases in the order of O₂ < C₂H₂ < C₂H₄ < CO < H₂ < CO₂ < N₂ while almost all metals (with exception for Au)

chemisorb oxygen, only the most active groups of metals (group A) chemisorb nitrogen.

1.5.2 Chemisorption and surface area of metals

The number of chemisorption sites can be measured in the following manner. A chemisorbing molecule which binds with a known stoichiometry to a surface site can act as the probe of the surface. For supported metal catalysts, this selective chemisorption of molecules on metal surface sites can be monitored by:

- (a) measuring the equilibrium uptake of gas phase molecules by the surface in a closed system (termed static or volumetric chemisorption);
- (b) detecting how many calibrated pulses of chemisorbed molecules are taken up by the surface (pulse chemisorption); or
- (c) counting chemisorbed molecules as they desorb from the surface upon heating (temperature programmed desorption).

The first two techniques are performed under isothermal (most often at ambient temperature) conditions and have been widely used to estimate the metal surface area and metal dispersions on the support, i.e., the number of chemisorbing sites. The third technique, one in a family of temperature programmed techniques for catalyst characterisation, can provide information on both of the parameters of importance, the strength and the number of chemisorbing sites.

The choice of hydrogen as an adsorbate for measuring the surface area of the metallic part of a catalyst has many advantages. ASTM committee D-32 [35], in general, recommended hydrogen as the chemisorbing molecule, since it is chemisorbed mainly on the metallic part of the surface and the uptake by the non-

metallic part (i.e. support) is relatively small in most cases. Physical adsorption of hydrogen may take place over both the metallic and the non-metallic part of the catalyst, but in carrying out the measurement at ambient temperature and pressure, the extent of the physically adsorbed layer can be neglected due to the very small adsorption enthalpy of hydrogen.

The use of hydrogen chemisorption for surface area measurement requires knowledge of the chemisorption stoichiometry, X_m , at monolayer coverage, which is the average number of surface metal atoms associated with the adsorption of each adsorbate molecule and also the number of metal atoms per unit area of surface, n_s . In the case of monolayer chemisorption, if n_m^s is the total adsorbate uptake expressed in molecules, the total surface area, S_H is given by

$$S_H = n_m^s X_m / n_s \quad (1.10)$$

The number of surface atoms per unit area of polycrystalline metal surface, n_s is not exactly known, but assumed from equal proportions of the main low index planes (equal proportions of the (111), (110) and (100) planes). Based on the morphology of small metal crystallites by electron microscopy, it is concluded that for fcc metals the equilibrium shape corresponds to the exposition of 70% (111) planes, 25% (100) planes and 5% (110) planes. The n_s numbers based on this hypothesis are also shown in Table 1.3.

Table 1.3 The number of surface atoms per unit area of polycrystalline surface, n_s for some metals active in catalytic hydrogenation [35]

Metal	$N_s (\times 10^{10}) \text{ per m}^2$	
	Equal proportions of (111), (110) and (100) planes	25%(100), 5%(110), 70%(111) planes
Cobalt	1.51	-
Nickel	1.54	1.75
Platinum	1.25	1.42
Palladium	1.27	1.45
Ruthenium	1.63	-
Iridium	1.30	1.48
Rhodium	1.33	1.55
Copper	1.47	1.67
Osmium	1.59	-

Generally, for the chemisorption of hydrogen up to full coverage, X_m , the average number of surface atoms associated with the adsorption of one adsorbed hydrogen molecule is supposed to be 2. For the (111) plane of fcc metals $X_m = 2$ is a realistic choice.

The total adsorbate uptake, n_m^s , is also subject to uncertainties. The largest amount of hydrogen uptake (strong chemisorption) takes place at a pressure below 1 torr. Above that pressure an uptake of weakly chemisorbed hydrogen is found,

mostly in the order of 20 to 25% of the strongly held monolayer. Note that the X_m value of 2 refers to the strongly chemisorbed hydrogen only. In many cases small metal crystallites are firmly attached to the support by chemical bonds. Hence, the value of n_s is strongly influenced by the support/particle interactions. This leads to the occurrence of the phenomenon of strong metal-support interaction that may even totally suppress any form of hydrogen chemisorption. The presence of the support may also give rise to hydrogen spillover, on account of which the hydrogen uptake may be much higher than expected.

1.5.3 H₂ chemisorption on metals

The ideal method for measuring monolayer H₂ adsorption capacity of supported metals would involve reproducible, convenient and rapid measurement using an apparatus that is easily and economically fabricated. It must account for hydrogen that is either reversibly or irreversibly chemisorbed on the metal while excluding chemical and physical adsorptions on the support. Finally, it should provide a mean of circumventing the kinetic limitations of highly activated adsorption. Of course, the measurement of an adsorbed monolayer can only be realized in the absence of surface contaminants, such as carbon, sulfur and/or reduced support moieties.

Adsorption of an H₂ molecule on base and noble metals generally occurs by dissociation to two hydrogen atoms each of which is assumed to adsorb onto one metal site. Moreover, the 1:1 stoichiometry has been verified experimentally for H-atom adsorption on metals atoms in quite a number of supported catalyst systems. In the standard ASTM (ASTM D3908-82) procedure for Pt/Al₂O₃ hydrogen is adsorbed

on a clean metal surface at 25 °C. The catalyst is first calcined at 400 °C to remove organic contaminants. It is then treated in dilute H_2 at 400 °C to reduce the surface oxide to the metal state. The sample is next evacuated at 380-390 °C to remove adsorbed hydrogen from the surface and then cooled to room temperature, and the measurement is initiated. The chemisorbing gas is then titrated incrementally onto the catalyst at 25 °C and the pressure is noted after each incremental increase, allowing sufficient time to reach equilibrium. When there is no further adsorption with increasing pressure (flat portion of Figure 1.11), it is assumed that the catalytic surface is saturated with a monolayer of adsorbate.

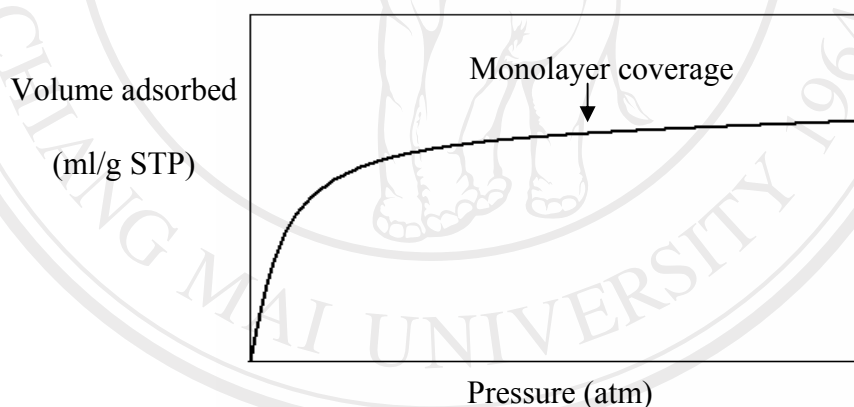


Figure 1.11 Typical static, volumetric chemisorption isotherm (adapted from [27])

By measuring the amount of gas adsorbed and knowing its stoichiometry of adsorption on the surface, the number of surface metal sites can be determined. It is sometimes necessary to measure the chemisorption contribution from the carrier

(typically small) without metal to provide a correction for the carrier in the following reaction:



Metal dispersion (fraction of metal exposed) can be estimated from the H_2 chemisorption uptake, i.e. the number of gas atoms chemisorbed at monolayer coverage divided by the total number of metal sites present in the catalyst times 100 is defined as the metal dispersion:

$$\% \text{dispersion} = \frac{N_s (\text{atoms of gas adsorbed})}{N_T (\text{total number of metal atoms present})} \quad (1.12)$$

By approximating a value for the cross-sectional area of a surface metal atom based on an assumed geometry, its surface area and average particle size can be calculated. If crystallites containing Pt are assumed to be spherical with an average diameter d (nm), the number of surface atoms is equal to the area of the particle divided by the cross-sectional area of an individual Pt site

$$N_s = \frac{\text{particle area } (\pi d^2)}{\text{area per Pt site}} \quad (1.13)$$

The number of Pt surface sites, N_s is experimentally determined from the number of H atoms chemisorbed. Chemisorption procedures using H_2 and other

probe gases have been applied to the study of many supported metals including Pt, Pd, Rh, Ir, Fe, Ni and Co [36].

1.5.4 Platinum catalysts

Supported platinum catalysts are one of the widely used in the industry. The supports may vary from alumina, to silica, activated carbon or ion exchanged in zeolitic catalysts. For the determination of platinum dispersion hydrogen chemisorption, in general, provides the best method, but optimum conditions for various systems need to be established experimentally. When it can be done without an unreasonably large contribution from adsorption on the support, the measurement of the dispersion of platinum by hydrogen chemisorption is preferably done at 273-300 K and at pressures up to about 0.2 kPa. It is fairly well founded to have the basis of one hydrogen atom adsorbed per surface platinum atom ($X_m = 2$) for the entire platinum size range.

The complications are that for many group VIII metals, strong chemisorption is followed by weak chemisorption and distinguishing between the two adsorption forms is one of the main problems. Temperature Programmed Desorption (TPD) technique offers the possibility of separating the weakly chemisorbed hydrogen from the strongly held type. The problem becomes more complicated by the occurrence of hydrogen spillover. This occurrence leads to a dramatic extent in hydrogen adsorption on platinum/carbon catalysts. From the experimental value of adsorbed hydrogen atoms the total numbers of platinum atoms present in the specimen may exceed by a factor of 3 to 10.

1.6 Nature of adsorbates on surfaces [35]

The interaction of CO with surface metal atoms gives rise to several different adsorption complexes such as linear, bridged and triple bonded CO molecules, in addition to dissociation into C and O atoms. In general, CO adsorbs dissociatively on reactive surfaces of metals (e.g. alkali metals, Ti and rare earth metals) from the left-hand side of the periodic table and in molecular form on surfaces of the metals from the right hand side of the d-block (e.g. Cu, Ni and Ag). For majority of transition metals, the nature of the adsorption is both dissociative and molecular which is very sensitive to the surface temperature and surface structure.

1.6.1 C-O stretching bands

A typical example cited widely to illustrate this aspect is the adsorption of CO molecules on transition metals. Different possible modes of CO chemisorption on supported transition metals and the associated C-O stretching frequencies are shown in Figure 1.12.

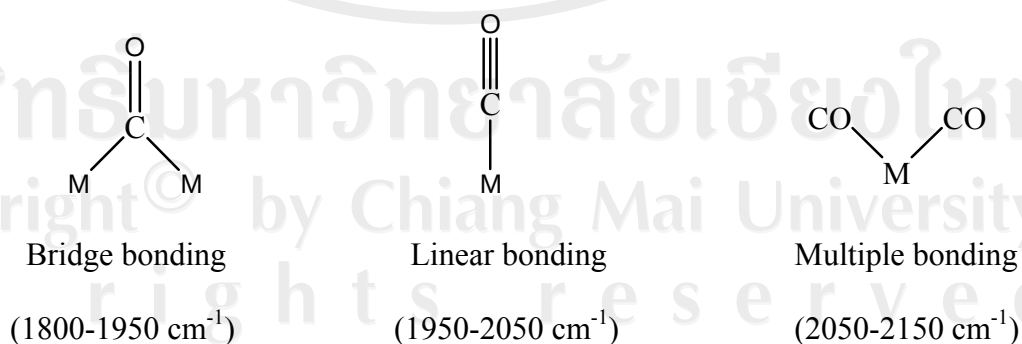


Figure 1.12 C-O stretching frequencies [35]

The actual C-O stretching vibrational frequency of these adsorption modes is found to depend upon various factors such as the nature of the adsorbent metal (M) and the adsorbate pressure. The shift is depending upon the surface coverage where the interaction between the adsorbate through dipole-dipole coupling decides the extent of frequency shift. Certain group frequencies which are IR inactive in normal state may become IR active on adsorption of a gas on catalyst surface.

Adsorption of carbon monoxide on the silica-supported platinum led to the appearance of only one adsorbed species, which show by a spectral band at 2073 cm^{-1} . In case of the silica-supported sample, only one band was observed at all surface.

1.6.2 Hydroxy group IR bands

Similarly, the frequency of the hydroxyl group (OH) is found to depend on the number of metal atoms on a catalyst surface to which oxygen atom is bound. Coordination number of 1 to 4 for hydroxyl groups are revealed in many cases. Schematic representation of differently bounded hydroxyl groups and their frequency range are given as follows. A sharp IR absorption band in the $3750\text{--}3745\text{ cm}^{-1}$ range is normally attributed to isolated silanol $[\text{-Si-OH}]$ on external surfaces. Another prominent band at $\sim 3611\text{ cm}^{-1}$ is identified with bridging OH groups, which serve as active sites in acidic function on zeolites. The actual frequency of this band depends on the nature of the zeolite and Si/Al ratio. The band appearing at $3720\text{--}3700\text{ cm}^{-1}$ is reported to arise due to silanol groups occurring at internal sites, where the weak electrostatic perturbations cause a downward shift and broadening of the IR stretching bands. The very broad band at $\sim 3500\text{ cm}^{-1}$ is ascribed to strong hydrogen-bonded interaction.

1.7 BET surface area [27, 37]

The specific surface area (in m^2/g) of a catalyst or a support material can be determined by the proven Brunauer, Emmett and Teller (BET) method. The volume of a gas (usually N_2) that gives monomolecular coverage is measured, allowing the total surface area to be calculated. The equilibrium isotherms are of the form shown in Figure 1.13.

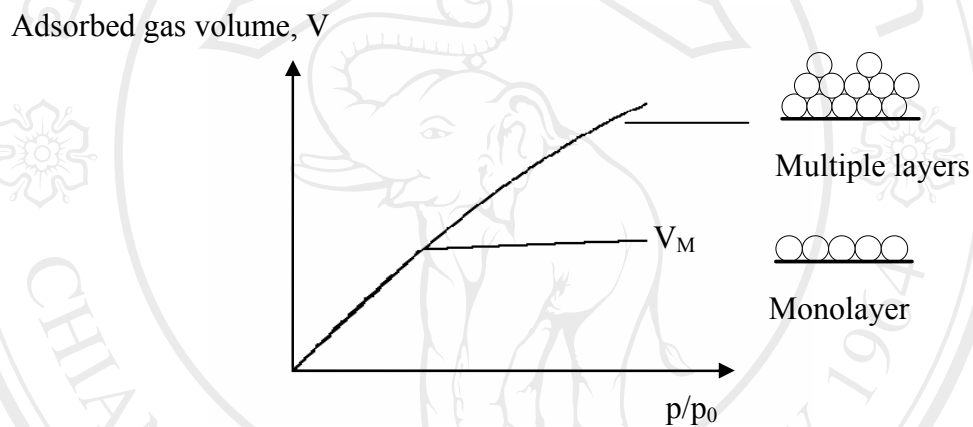


Figure 1.13 The equilibrium isotherms of BET specific surface area (adapted from [37])

In Figure 1.13 the adsorbed volume is plotted against p/p_0 (p = pressure, p_0 = saturation pressure). At low pressures monolayer adsorption obeys the Langmuir equation:

$$\frac{V}{V_M} = \frac{K (p/p_0)}{[1 + K (p/p_0)]} \quad (1.14)$$

V_M = volume of the monolayer, K = constant

However, above about $p/p_0 = 0.1$, multilayer adsorption becomes important. A theoretical model for describing such adsorption processes was developed by Brunauer, Emmett, and Teller, who familiar BET equation 1.15. In 1938 this model was the first successful attempt to describe the multilayer adsorption.

$$\frac{V}{V_M} = \frac{cp}{[p_0 - p][1 + (c-1)(p/p_0)]} \quad (1.15)$$

c includes the heat adsorption, condensation and is a constant for a particular class of compounds with values of over 100.

1.8 X-ray diffraction [33, 38-39]

X-Ray diffraction (XRD) was used to investigate the bulk phases present in the sample and to determine the ageing-induced solid-solid phase transformations. X-rays are energetic enough to penetrate into the material and their wavelengths are of the same order of magnitude as interatomic distances in solids. Thus, a collimated beam of X-rays is diffracted by the crystalline phases in the sample according to Bragg's Law (equation 1.16).

Subsequent developments enabled the quantitative determination of the structure of crystalline materials, leading to a rapid increase in the understanding of the role of crystal structure in material properties and, as a consequence, rapidly advancing materials science.

A common laboratory source of X-rays consists of an evacuated tube in which electrons are emitted from a heated tungsten filament, and accelerated by an electric

potential (typically several tens of kilovolts) to impinge on a water-cooled metal target. The interaction between the electrons and the target leads to the emission of X-rays; some having a wavelength characteristic of the target, and some having a continuous distribution of wavelengths between about 0.05 nm and 0.5 nm (the so-called white radiation). For most experiments, characteristic radiation is selected (using a filter or Bragg reflection from a suitable crystal) because of its intensity and accurately known wavelength.

Bragg's law is the cornerstone of X-ray diffraction analysis; it allows to make accurate quantification of the results of experiments carried out to determine the crystal structure. It was formulated in 1912 by W.L. Bragg, in order to explain the observed phenomenon that crystals only reflected X-ray at certain angles of incidence. An X-ray incident upon a sample will either be transmitted, in which case it will continue along its original direction, or it will be scattered by the electrons of the atoms in the material. All the atoms in the path of the X-ray beam scatter X-rays. In general, the scattered waves destructively interfere with each other, with the exception of special orientations at which Bragg's law is satisfied.

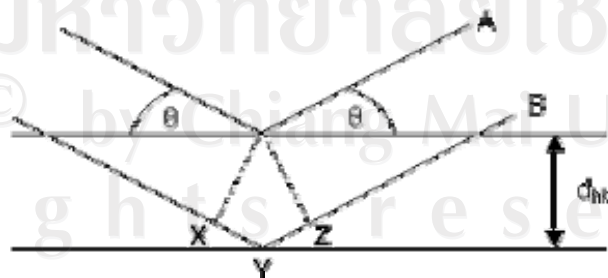


Figure 1.14 The diffraction of X-rays by crystal planes [39]

The geometry of the Bragg condition is remarkably simple, and leads to the powerful result of the Bragg law as shown in Figure 1.14.

Hence,

$$n\lambda = 2d\sin\theta \quad (1.16)$$

Where, λ is the wavelength of the X-rays, d is the distance between two atomic planes in the crystalline phase, n is the order of the diffraction and θ the incoming diffraction angle. In order to consider the general case of hkl planes, the equation can be rewritten as:

$$\lambda = 2d_{hkl} \sin\theta_{hkl} \quad (1.17)$$

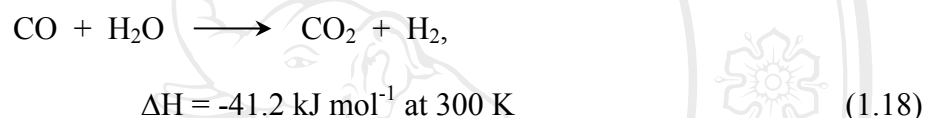
since the d_{hkl} incorporates higher orders of diffraction i.e. n greater than 1. The angle between the transmitted and Bragg diffracted beams is always equal to 2θ as a consequence of the geometry of the Bragg condition. This angle is readily obtainable in experimental situations and hence the results of X-ray diffraction are frequently given in terms of 2θ .

Single crystal X-ray diffraction, although simple, is often very difficult to arrange in practice since it requires a single crystal to be grown. This may be difficult for some samples, and is impossible for multi-phase samples. Additionally as mentioned in the previous section, there is a very precise requirement on the alignment of the crystal. Diffraction experiments can also be carried out using either

a powder, or more commonly a polycrystalline sample. This ideally results in all possible orientations appearing in the sample.

1.9 The Water gas shift reaction

The water gas shift (WGS) reaction is an inorganic chemical reaction in which water and carbon monoxide react to form carbon dioxide and hydrogen (water splitting). The overall WGS reaction is represented as equation 1.18 [40-46]



The water gas shift reaction is part of steam reforming of hydrocarbons and is involved in the chemistry of catalytic converters. It was discovered by an Italian physicist Felice Fontana in 1780 [33]. In recent years, there has been a renewed interest in the WGS reaction due to the need for low-cost pure hydrogen production by further developments of hydrocarbon steam-reforming technologies in which natural gas and other bio mass-derived liquid fuels, such as ethanol, sugars and bio-oil can efficiently be used to produce syngas and hydrogen [44].

While this reaction could be used to produce hydrogen, the high temperatures requirement makes it cost-prohibitive. The generation of hydrogen itself has significant promise as a replacement clean burning fuel itself; however this reaction is usually done via the byproducts of fossil fuel combustion. The carbon monoxide can also be generated by bogs or other waste regenerative means.

Although the WGS reaction involves only four small molecules, the reaction mechanism is quite complex [46]. The role of the WGS reactor in such systems is to provide primary CO cleanup and secondary hydrogen production. The maximum CO conversion which can be achieved in a WGS reactor is limited by chemical equilibrium. It is important to develop stable and selective catalysts with sufficiently high activity at low temperatures. Among the various metal/support combinations investigated for the low temperature WGS reaction, ceria-supported precious metal catalysts seem to be a promising candidate for fuel cell applications. Extensive work has been devoted to the catalytic oxidation of H₂ and CO on transition metals, and a number of microkinetic models, consisting of elementary-like reaction steps, have been proposed, especially on Pt. Microkinetic models that could be used for the simultaneous modeling of WGS, preferential oxidation (PROX) and partial oxidation (POX) reactor are still lacking [47-52]. The reverse water gas shift (RWGS) reaction has recently found a possible application in *in situ* Resource Utilization on Mars to provide oxygen for fuel and also in other works [5, 7, 53].

The essential role of the industrial WGS reaction is to increase the production of hydrogen for refinery processes, bulk storage and redistribution. This includes the need for gases of appropriate H₂/CO ratios in the production of organic bulk chemicals such as ammonia, methanol, and alternative hydrocarbon fuels through Fischer-Tropsch synthesis. These gas mixtures applied in industry are usually referred to as synthesis gas or syngas and are produced in large scale facilities by high temperature reaction of carbonaceous materials in presence of water or oxygen where supported nickel catalysts are in use or by gasification of coal.

In most fuel processor designs of the WGS reaction must deliver a CO concentration of <1% to the selective CO oxidation reactor. Any further reduction in CO concentration causes the load on the CO oxidizer. High temperature fuel cells are not as dependent on the WGS shift reaction to reduce CO since they are able to withstand the high CO concentrations expected from the reforming reaction. The WGS reaction is very desirable for fuel processing as it provides two benefits. In addition to effectively reducing the CO concentration, a mole of H₂ is produced for every mole of CO that is converted in the WGS reaction (equation 1.18) [54].

1.9.1 Mechanisms and kinetics

There are generally two reaction mechanisms proposed in the literatures for the WGS reaction, Associative and Redox [42, 52, 55-59]. In the first one a formate species is formed which then decomposed forming CO₂ and H₂. The redox mechanism consists of a surface oxidation followed by surface reduction.

Based on the kinetic results, two types of mechanisms were proposed. The oxidation-reduction, or regenerative mechanism of Rideal-Elay type, in which water oxidizes the surface and CO re-reduces the oxidized surface. Others describe a bi-functional process where the adsorbed CO on the precious metal or mixed metal oxide is oxidized by the support and then water fills the support oxygen vacancy [54].



Where $*$ is an active metal site. The multi-step Langmuir-Hinshelwood type or associative mechanism where adsorbed or dissociated water forms reactive hydroxyl groups that combines with CO to produce a formate that decomposes to CO_2 and H_2 . The bi-functional nature where CO adsorbed on the reduced metal migrates to react with hydroxyl groups to produce the formate intermediate. FTIR analysis has been commonly used to confirm the presence of the formate intermediate:



The rate-determining step was found to be the decomposition of the formate. An increase in the water partial pressure increased the rate of formate decomposition and the activation energy decreased.

1.9.2 Role of WGS for automotive exhaust gas cleaning systems [54]

In contrast to conventional base metal catalysts, supported precious metal catalysts have been known to be active for the WGS reaction for many years with early research performed in 1925 by Prichard and Hinshelwood [60] who studied the reverse WGS reaction over supported Pt. Much attention was focused on the WGS

reaction as it applied to automotive exhaust catalysts with respect to CO emissions in the 1970s and 1980s.

Many researchers reported that CeO_2 promoted the WGS reaction [61]. It was shown that Pt was the most active for WGS reaction followed by Pd and Rh on alumina and the activity was improved with the incorporation of 12% CeO_2 with alumina [61]. Currently CeO_2 is generally added to three-way catalysts in order to promote the WGS reaction and to store oxygen under lean conditions for use under rich conditions. The literature provided useful information for the development of precious metal WGS catalysts for fuel processing but there are differences that must be noted. Most WGS activity evaluations were made with respect to exhaust catalyst typically were studied in an oxidative atmosphere and at temperature $> 400\text{ }^\circ\text{C}$. The effect of CO_2 and H_2 were not often considered. The WGS fuel processing environment is more reducing where the partial pressures of CO_2 and H_2 are much greater and the operating temperatures are generally run lower between $180\text{--}450\text{ }^\circ\text{C}$.

1.10 Catalytic kinetics

1.10.1 Kinetics in heterogeneous catalysis [62]

A physio-chemical understanding of catalytic processes is thus essential for proper reactor modeling. According to the very definition of catalysis it is considered as a kinetic process, and thus the reliable kinetic models that describe the rate of catalytic reactions are of vital importance for solving applied problems in mathematical modeling, design and intensification of chemical processes. The necessity of kinetic investigations in heterogeneous catalysis is closely connected to the tasks, which a chemical engineer has to deal with, i.e. proper reactor design,

evaluation of the side reactions and the impact of dynamic effects on reactor performance. Any reactor design thus starts from reaction kinetics and therefore from the reaction mechanism, which means understanding of the reaction on a molecular level. Reaction kinetics is the translation of the understanding of the chemical process into a mathematical rate expression that can be used in reactor design.

Kinetic modeling used for process development and process optimization has historical tradition. Quite often power law models are still used to describe kinetic data. Such phenomenological expressions, although useful for some applications, in general are not reliable as they do not predict reaction rate, concentration and temperature dependence outside of the range of the studied experimental conditions. Thus, in catalysis due to the complex nature of this phenomenon adsorption and desorption of reactants as well as several steps for surface reactions should be taken into account. Models based on the knowledge of elementary processes should provide a reliable extrapolation outside of the studied interval and also make the process intellectually better understood.

For some reactions the rate is independent on particle size, shape and other physical characteristics, while for structure sensitive reactions the rate depends more on the detailed surface structure.

The temperature dependence of heterogeneous catalytic reactions was partially addressed above where it was demonstrated that in general activity increases with temperature, however, increased temperature shortens the catalyst life time and typically increases the rate of undesired reactions.

1.10.2 Microkinetic modeling [62]

Microkinetic modeling is a framework for assembling the microscopic information provided by atomistic simulations and electronic structure calculations to obtain macroscopic predictions of physical and chemical phenomena in systems involving chemical transformations. In such approach the particular catalytic reaction mechanism is expressed in terms of its most elementary steps. In contrast to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formulations, no rate-determining mechanistic step (RDS) is assumed.

Microkinetic models are much more widely applicable than LHHW traditional models which assume as an RDS, since the RDS can change with reaction conditions. Since all postulated elementary steps are included explicitly, accurate rate parameters for all of the forward and reverse reactions are needed to solve the equations comprising in the model. This requirement greatly increases the amount of information needed to create a microkinetic model. Often, the information needed to create a microkinetic model can not be determined from one set of experiments but requires the compilation of information from many different experiments and some theoretical investigations. The wider utilization of microkinetic models is somewhat retarded by the vast amount of information needed about interactions of chemical intermediates with complex, heterogeneous catalysts. The microkinetic approach has been applied to numerous diverse chemistry including cracking, hydrogenation, hydrogenolysis, oxidation reaction and ammonia synthesis.

Microkinetic modeling assembles molecular-level information obtained from quantum chemical calculations, atomistic simulations and experiments to quantify the kinetic behavior at given reaction conditions on a particular catalyst surf.

1.11 Mathematical treatment of DRIFTS spectra

The reason why the absorbance was used to calculate surface concentration (rather than the Kubelka-Munk function, usually used when handling diffuse reflectance data) is discussed. The typical single channel FTIR spectra used to determine the nature and amount of species present over the sample are shown in Figure 1.15. The upper spectrum, which is used as background, is that of the solid (i.e. the 2%Pt/CeO₂) after reduction. The bottom spectrum is that of the same solid under reaction stream (i.e. CO₂/H₂/Ar). The band at 2062 cm⁻¹ was used to quantify the carbonyl ¹²CO (ads) species.

The detector signal for the mirror background, i.e. I_0 , and that for the sample, i.e. I , are used to calculate the sample reflectance $R_\infty = I / I_0$ (the reflectance is the equivalent of the transmittance $T = I / I_0$ used in the transmission mode). The reflectance of the sample under CO can also be calculated as $R = I_{\text{ads}} / I_0$.

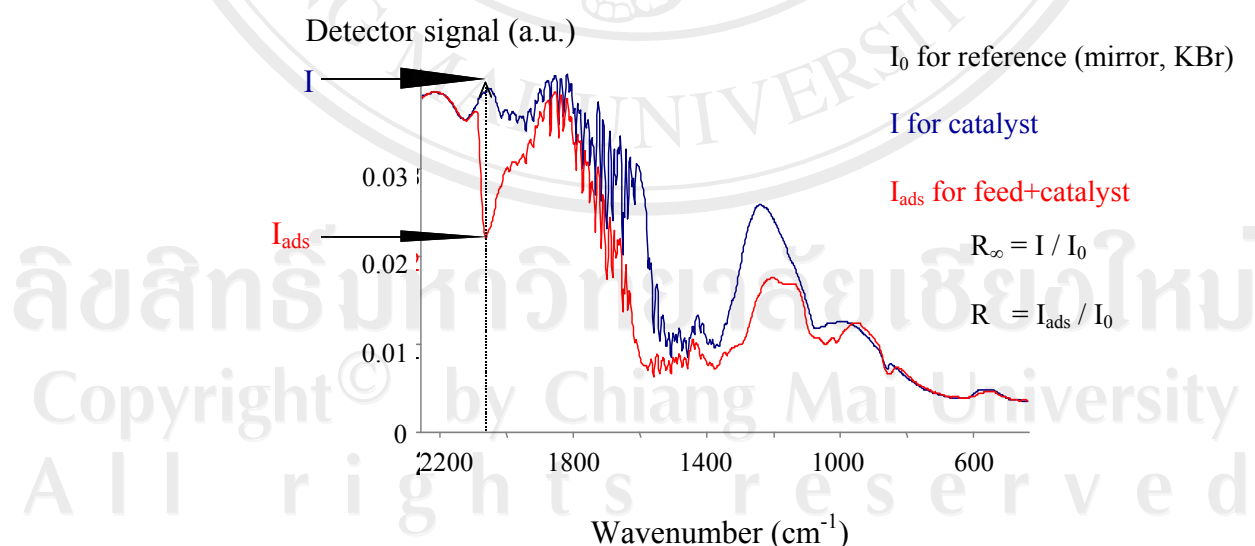


Figure 1.15 Single channel FTIR spectra of the fresh solid and that with surface adsorbed species

The basis of the diffuse reflectance theory used to quantify the concentration of a solid solute in a non-absorbing matrix was developed by Kubelka and Munk [63] and widely applied to the mid-IR regions [10] and sometimes to the UV-Vis and near-IR regions [13]. The Kubelka-Munk formula (equation 1.26) relates the absolute reflectance R_∞ of the scattered radiation (R_∞ = intensity scattered divided by that of the incident radiation) to the sample absorption and scattering coefficients k and s , respectively.

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \quad (1.27)$$

This equation refers to a semi-infinite thick sample, a condition that is achieved in practice with catalyst beds thicker than a couple of millimetres for typical catalytic materials [64]. The incident intensity is usually not known and difficult to measure. Therefore, a typical DRIFTS experiment usually consists, firstly, in measuring the diffusively reflected intensity I_∞ (ref) over a reference sample (poorly absorbing and highly scattering medium such as finely divided KBr particles for the mid-IR [10]) and, secondly, measuring the intensity I_∞ (sample) over the sample of interest. However, the moisture level of reference salts and the particle size of samples will have an effect on the medium absorptivity and scattering properties [10], respectively. Therefore, experiments carried out using a 180° configuration (Spectra-Tech Collector in this thesis) usually rely on using a flat perfectly reflecting metallic mirror as reference, which allows measuring with a good precision of the incident intensity (otherwise largely underestimated when using KBr with commercial cells,

which do not comprise a full integration sphere). The value of the ratio $I_{\infty}(\text{sample}) / I_{\infty}(\text{ref})$ is then taken as an approximate value for R_{∞} . For a solute of absorptivity $k = 2.303\varepsilon C$, where ε is the molar absorptivity and C the solute concentration in a non-absorbing matrix, the Kubelka-Munk function $f(R_{\infty})$ is directly proportional to C :

$$C = \text{constant} \times f(R_{\infty}) \quad (1.28)$$

In practice, many of the conditions required for the Kubelka-Munk theory to apply are not often met, e.g. because of the presence of Fresnel (i.e. specular, mirror-like) reflection, matrix absorption, and non-uniform optical properties of the sample. Signal corrections can be made, even for non-diluted samples, but the data treatment is complex and the effect of the sample micro or nanostructure will also affect the scattering coefficient, making it difficult for comparison between differently prepared samples. In many cases, simple calibration curves have shown that the Kubelka-Munk equation is not linear with respect to the concentration of the solute, displaying a curved [13] or broken-line shape. Olinger and Griffiths [13] proposed that in the case of strongly absorbing matrices, such as that of most catalytic materials, the best linear representation of a solute concentration is given by $\text{Log} (1/R)$, noted “absorbance” by analogy with the absorbance = $\text{Log} 1/T$ measured in transmission IR:

$$C = \text{constant} \times \text{Log} \frac{1}{R_{\infty}} \quad (1.29)$$

Matyshak and Krylov [65] stressed that the quantification of adsorbates (as opposed to solutes) in DRIFTS measurement should actually be derived from a modified Kubelka-Munk function. Starting from equation 1.26, these authors simply added a term due to the absorbance of a surface species of surface concentration θ and absorptivity ε' when considering the reflectance R measured in the presence of the adsorbate:

$$f(R) = \frac{(1-R)^2}{2R} = \frac{k + \varepsilon' \theta}{s} \quad (1.30)$$

By combining equations 1.26 and 1.29, it can be shown that the surface concentration θ is proportional to a simple function of R_∞ and R [65], which now named Matyshak-Krylov function $MK(R, R_\infty)$ for convenience as:

$$MK(R, R_\infty) = \frac{(R_\infty - R)}{R_\infty} \left(\frac{1}{R} - R_\infty \right) \quad (1.31)$$

$$\theta = \text{constant} \times MK(R, R_\infty) \quad (1.32)$$

where R_∞ and R are the catalyst reflectance and the (catalyst + adsorbate) reflectance relative to the reference sample, respectively. It is worth mentioning that the Matyshak-Krylov function shown above is not, to the knowledge, available in any spectrometer software. Therefore, either the Kubelka-Munk or the absorbance (= Log

$1/R$) functions are typically used to represent surface species concentrations, although neither of those may be a perfect representation of surface concentration.

The variation of relative reflectance (R'), absorbance ($\log (1/R')$), and Kubelka-Munk function (equation 1.33), as a function of adsorbate concentration are given in Figures 1.16 and 1.17.

$$f(R') = \frac{(1 - (R/R_\infty))^2}{2(R/R_\infty)} = \frac{(1 - R')^2}{2R'}, R' = R/R_\infty \quad (1.33)$$

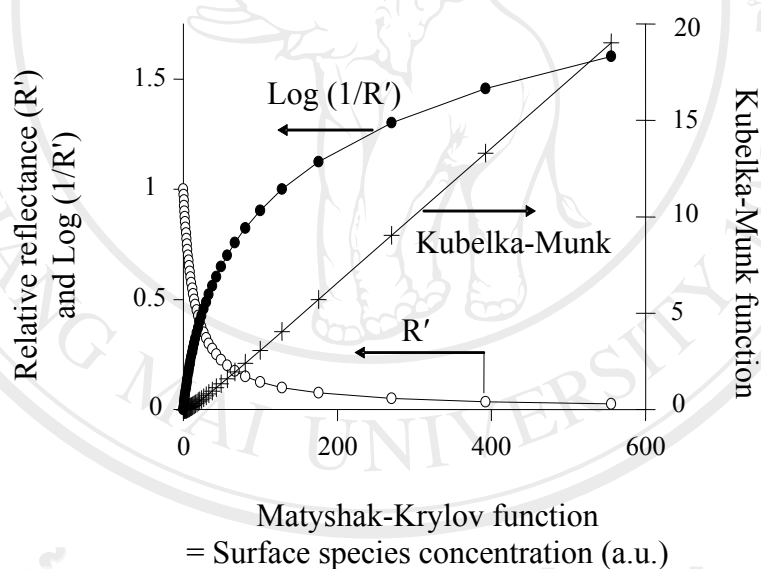


Figure 1.16 Theoretical values of (o) the relative reflectance R' , (●) $\log (1/R')$ and (+) the Kubelka-Munk transformation $f(R')$ as a function of the Matyshak-Krylov function.

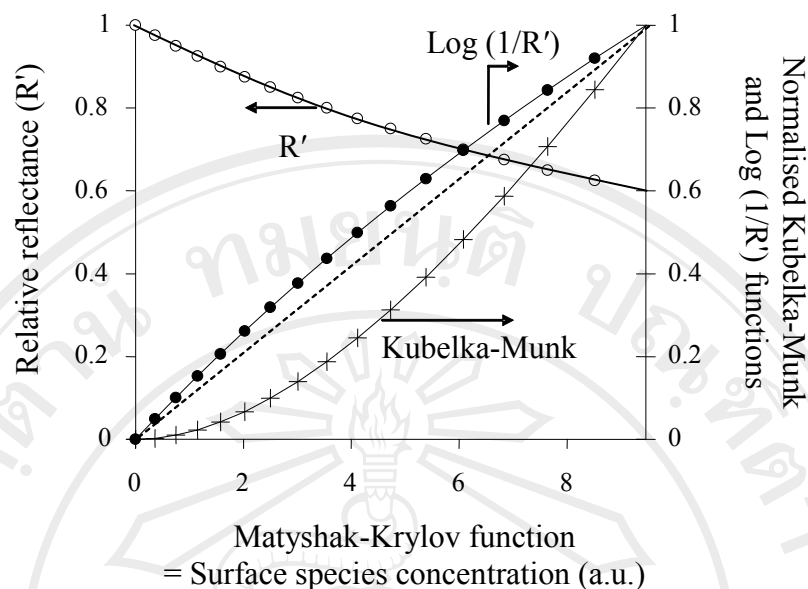


Figure 1.17 Detail of Figure 1.16, limited to relative reflectance R' values comprised between 1 and 0.6. For comparing the shape of the curves, the Kubelka-Munk function $f(R')$ and absorbance $= \text{Log}(1/R')$ were normalised using the corresponding value of these functions at $R'=0.6$. (the dashed line is an eye-guiding straight line).

The experiment is based in part on the adsorption of CO on Pt/SiO₂ at room temperature. Some absorbance spectra already reported elsewhere [24, 25] related to the reactivity of formate species over Pt/CeO₂ were re-used to allow comparing those with other intensity transformations.

1.12 Literature reviews

In 1991, the characteristics of diffuse reflectance (DR) infrared spectrometry for the study of adsorbed species were investigated by Van Every and Griffiths [12]. The adsorption of carbon monoxide on alumina-supported rhodium ($\text{Rh}/\text{Al}_2\text{O}_3$) catalysts was used as a model system. Activation of the catalysts was conducted *in situ* in the DR cell at 573 K under a flow of purified hydrogen for two hours, evacuating at 588 K for one more hour, and cooling the sample to ambient temperature at 10^{-6} Torr. The adsorbent was typically exposed to a carbon monoxide at pressures from below 1 milliTor to above 5 Torr. Band intensities of adsorbed species as they appeared in the Kubelka-Munk (KM) spectra were linear with surface coverage over a low coverage range but showed a negative deviation from linearity at high coverage. Reproducibility between different catalyst samples was affected by sample packing and treatment history.

In 2001, different spectroscopic methods were compared to quantitatively determine organic compounds adsorbed or grafted on silica by Pere and coworkers [15]. Transmission FTIR, diffuse reflectance (DRIFT) and UV (DRUV) spectroscopy were used to measure the concentration of adsorbed, *N*-propyl-*p*-benzoylbenzamide on silica in a KBr matrix. The diffuse reflectance spectra were treated according to the Kubelka-Munk theory.

A quantitative analysis of powdered (adsorbed / or grafted) samples was also possible by IR spectroscopy but in this case [15], the absorption of the support had to be taken into account. For DRUV, this method was useful whatever the nature of the adsorbate (i.e. chromophoric or not). The standard was made by mixing pure silica and KBr, both finely ground, and the adjustment was made on the wavenumber of 800

cm^{-1} . The DRIFTS spectra of ground samples appeared easier to process than the transmission spectra because of a better baseline and resolution. Although the DRIFTS signals obtained for non-ground samples (the spectral range below 1300 cm^{-1}) were less intense and resolved, their quantitative treatment could however be achieved. Moreover, sample preparation was much easier for DRIFTS spectra as no pellet was made. However, DRIFTS method due to a weaker signal than in transmission, the samples have to be more concentrated in the KBr matrix and the FTIR detector requires higher sensitivity.

In 2002, fast quantification of humic substances (HS) and organic matter (OM) by direct analysis of sediments was studied by Tremblay and Gagne [21], using DRIFTS spectroscopy. In this case, the developed DRIFTS could rapidly quantify sedimentary HS and total OM in the whole dry samples without the usual tedious extraction procedures. Under optimized conditions, the quantification of humic substances or total organic matter with DRIFTS was performed at a frequency of 2390 cm^{-1} . Potassium chloride (KCl) was used as a non-absorbing reference material for the spectroscopic background measurement. Powder KCl and fused quartz were used to dilute the humic acids. However, to ensure reproducible analyses, some operational conditions must be controlled as the collected energy, sample particle size, compaction and homogeneity.

In 2004, the spectrokinetic investigation of reverse water-gas-shift reaction was studied by Goguët and coworkers [2]. Also, in 2006, the *in situ* DRIFTS and the steady-state isotopic transient kinetic analysis (SSITKA) technique were investigated the reaction mechanisms and reported by Tibiletti and coworkers [24]. The reaction was elucidated over a 2% Pt/CeO₂ catalyst with the reaction mixture of gases, i.e.,

1% $^{12}\text{CO}_2$ +4% H_2 in Argon. Moreover, for the same reaction condition, on the reactivity of carbonate species on a Pt/CeO₂ catalyst was studied previously by Meunier and coworkers in 2005 [8].

A quantitative analysis of surface intermediates precursors of CO (g) could be integrated the area between the MS (Mass spectrometry) line of the tracer (He) and that of CO (g). In a similar manner, the quantity of surface intermediates releasing CO₂ could be calculated using the appropriate CO₂ MS signals.

Improving the linearity of DRIFTS for the quantitative analysis was represented by Samuels and coworkers in 2006 [66]. Under Kubelka-Munk (KM) theory linearity was better afforded than that reduced in log (1/R) units. However, baseline position variance in the KM data space resulted in observed peak intensity changed that was proportional to the observed offset. They validated their KM correction strategy by repeating the experiment using simpler systems of pure caffeine in potassium bromide. The numerical preprocessing included conventional multiplicative scatter correction (MSC) coupled with a baseline offset correction that facilitated the use of quantitative diffuse reflection data in the KM formalism for the quantitation of contaminants in a complex soil matrix, but was also applicable to more fundamental diffusion. Also, a method to improve linearity of Diffuse Reflection Mid-IR was reported by Averett and Griffiths in 2006 [20]. Binary mixtures of caffeine and KCl were used as the model system. Both, baseline correction and MSC were needed if linear plots were essential needed.

1.13 Research objectives

1. To develop the quantitative analysis of DRIFTS spectra over catalytic materials
2. To learn, both theoretical and experimental considerations to assess the most appropriate mathematic transformation to be evaluated and correlated the adsorbate surface concentration and DRIFTS signals

1.14 Usefulness of the Research (Theoretical and/or Applied)

1. Modified and controlled commercial DRIFTS cell combined with an advanced DRIFTS signal integration and treatment to yield fully quantitative information on the true steady-state reactivity of adsorbates.
2. The method represented a more advanced tool that can be used in all catalytic materials for the rapid quantitative analysis.