

TWO DIMENSIONAL MODELLING FOR CATALYTIC COMBUSTION

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ABSTRACT

Potential of catalytic combustion as a method of NO_x emission in gas turbine application have been realized, but research in this area never been higher. Catalysts properties assist chemical reactions by affecting the rate of reaction. It allows fuel oxidation at temperature below flammability limit. In this research, simulation using CFD commercial code in catalytic combustion needed and using a simple steady state laminar flow, thus, a 2D catalytic combustion was modeled and simulated. Using Fluent software and the mathematical models available for species transport and wall surface reaction, the results provided by Dogwiler of The Paul Scherrer Institute in Switzerland, been compared qualitatively. The effect of some design parameters, such as the gas mixture inlet velocities and equivalence ratio on the heterogeneous reaction were validate

ABSTRAK

Potensi pembakaran berpemangkin sebagai kaedah untuk mengurangkan NOX di dalam turbin gas telah disedari, tetapi kajian di dalam bidang ini tidak pernah meningkat. Sifat pemangkin membantu tindakbalas kimia dengan mempengaruhi kadar tindakbalas. Ia membenarkan bahan api teroksida pada suhu di bawah had pembakaran. Di dalam kajian ini, simulasi menggunakan kod komersial CFD di dalam pembakaran berpemangkin diperlukan dan menggunakan "*steady state laminar flow*" yang ringkas, oleh itu sebuah dua-dimensi pembakaran berpemangkin telah dimodel dan disimulasi. Menggunakan perisian FLUENT dan model matematik untuk pindahan spesis dan tindakbalas pada permukaan dinding, keputusan yg disediakan oleh Dogwiler dari The Paul Scherer Institute di Switzerland telah dibandingkan dengan tepat. Pengaruh beberapa parameter rekaan, seperti kelajuan masukkan campuran gas dan nisbah kesetaraan pada tindakbalas heterogen disahkan.

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CHAPTER 1

INTRODUCTION

1.1. Background

Since the 1970's, engineers and scientists have started to realize the potential of using catalytic combustion as a method of NO_x reduction in gas turbine applications. Today, the number of R&D projects in this area in all industrialized countries has probably never been higher. With the properties of catalysts, which assist chemical reactions by affecting the rate of reactions, its usage in the combustion process could allow fuel oxidation to take place at temperatures well below the flammability limit of the fuel. Using FLUENT software and the mathematical models available for species transport and wall surface reaction, the results provided by Dogwiler can thus be use to validate and verify laminar models that can then be applied to these problems with confidence in the engineering sector

The use of combustion by man is old indeed. In fact, man's discovery of fire predates written history. Even today, combustion of fuels in air represents man's principle source of heat and power although now man burns mostly fossil fuels rather than woods. By conventionally, combustion means flames, has been recognized to generate high levels of pollutants. The caveman must have been driven out of his cave at times by a smoky fire and thus made aware of the pollution potential combustion. Soon, man learned to put chimneys on his fireplaces. It was

not until the advent of cities, however that man realized he could pollute outdoors also.

1.2. Problem Statement

Smog produce by human nowadays from factory and vehicles contains hazardous chemical that can affect human life. But the number of R&D projects in this controlling the pollution in all industrialized countries has probably never been higher. Therefore a catalytic combustion as a NO_x emission system is really needed to reduce the chemical pollution in air. But the cost to design the catalytic combustion to do testing is high and takes time. Furthermore, a catalytic combustion has difficult parameter that need to be analyzed. Thus, it is very suitable to simulate the catalytic combustion in CFD before it can be used.

1.3. Objective.

- 1.3.1. To compare with Dogwiler replicate qualitatively.
- 1.3.2. To see the effects of some design parameters, such as the gas mixture inlet velocity and equivalence ratio on the heterogeneous reaction.
- 1.3.3. To do numerical analysis to the equation involve.
- 1.3.4. To do the simulation process using CFD package.

1.4. Scope of study

- 1.4.1. Simulation using CFD commercial code in catalytic combustion.
- 1.4.2. Using a simple steady state laminar flow.

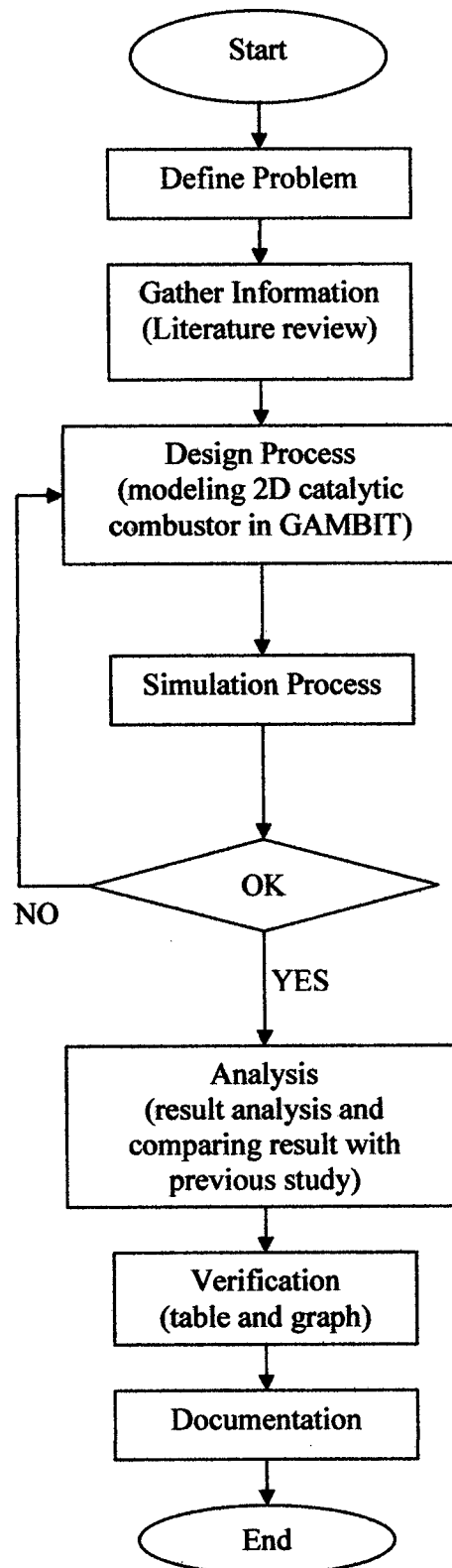


Figure 1.2 Project Flowchart

CHAPTER 2

LITERATURE REVIEW

2.1 Air Pollution

By the 1940 and 1950s air quality problems were experienced in some urban cities because of the increasing number of cars. This was especially noticeable in locations such as the Los Angeles' basin where temperature inversions trap and recycle polluted air. By the 1960s cars had been in large scale mass production for many years, and they gave personal mobility to an increasing range of people. But, oxidation of gasoline in the engine to CO₂ and H₂O was far from completely efficient, so the exhaust gas contained significant amounts of unburned hydrocarbons and lower levels of partially combusted products like aldehydes, ketones, and carboxylic acids, together with large amounts of CO. Unburned fuel and other hydrocarbons formed by pyrolysis, and various oxygenated species are referred to as "hydrocarbons" and designated HC.

In some American cities irritating photochemical smog became so frequent that air quality was a major health concern. The origin of these photochemical smog was two of the primary pollutants from cars. They were of concern in their own right, but they underwent photochemical reactions to generate ozone, a strong irritant, as well as low levels of other even more noxious compounds.

2.2.3 Fuel NO_x

Fuel NO_x is formed when fuels containing nitrogen are burned. Traditionally, most light distillate oils have had less than 0.015 percent nitrogen content by weight. However, these distillate oils may contain percentages of nitrogen exceeding the 0.015 threshold if they were produced with poorer quality crudes, thus can increase fuel NO_x formation.

2.3 Heterogeneous catalyst

A catalyst is added to a reaction system to alter the speed of a chemical reaction approaching a chemical equilibrium. Another reason for using catalyst is that it promote the production of a selected product.

A catalyst changes the activation energy, E_a , of a reaction by providing an alternate pathway for the reaction. The rate and rate constant k of a reaction are related to E_a in the following ways:

$rate = k * \text{function of concentration}$

$$k = Ae^{-E_a/RT} \quad (2.6)$$

Where A is a constant related to collision rates. Thus, a change in E_a changes the rate of a reaction.

A catalyst in a separate phase from the reactants is said to be a heterogeneous, or contacts catalyst. Heterogeneous catalysts provide a surface for the chemical reaction to take place on. In order for the reaction to occur one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb from the surface and diffuse away from the solid surface. Frequently, this transport of reactants and products from one phase to

another plays a dominant role in limiting the reaction rate. Understanding these transport phenomena and surface chemistry such as dispersion is an important area of heterogeneous catalyst research. Catalyst surface area may also be considered.

Homogeneous catalysis is a chemistry term which describes catalysis where the catalyst is in the same phase (solid, liquid and gas) as the reactants. Homogeneous catalysis, the catalyst is in the same phase as the reactant.

2.4 Introduction of Catalytic Combustion

Long time ago, this catalytic combustion was called surface-catalyzed combustion. It is used to purify emissions from gasoline and diesel engines. Under certain operating conditions, these engines can release substances that are environmental hazards, such as carbon monoxide (CO), nitrogen oxides (NO_x), and unburned hydrocarbons (also known as volatile organic compounds, or VOC_s). To convert these substances to more acceptable ones, catalytic combustors force the exhaust gas through a substrate, a ceramic structure that is coated with a metal catalyst, such as palladium or platinum. For gasoline engines, exhaust gases react with these metals, causing CO to be converted to CO₂ and NO_x to be converted to nitrogen and oxygen. For diesel engines, catalytic converters are primarily used to treat the NO_x compounds.

It is an efficient method for burning fuel in lean fuel air mixtures without significant formation of pollutants. This combustion also offers the potential for improved thermal efficiency and can even operate outside the flammability limits for flame combustion.

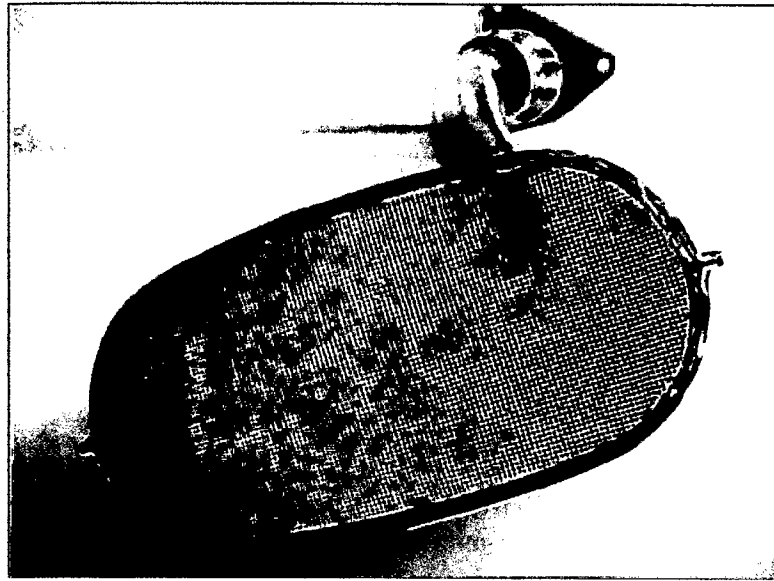


Figure 2.2 Sectioned view of a honeycomb type catalytic converter

As shown in the photograph in Figure 2.2, the catalytic converter is composed of a stainless steel shell which contains the ceramic honeycomb on which the catalytic active material is deposited. The ceramic honeycomb is surrounded by a thin layer of insulation fiber to maintain high gas temperatures and thus improve the catalytic reaction. In fact, this is the reason for the low temperature of the external surface of the steel shell. This insulation layer causes an important temperature drop between the internal and the external surfaces of the wall. Therefore, it is not accurate to assume that the temperature of both surfaces is similar.

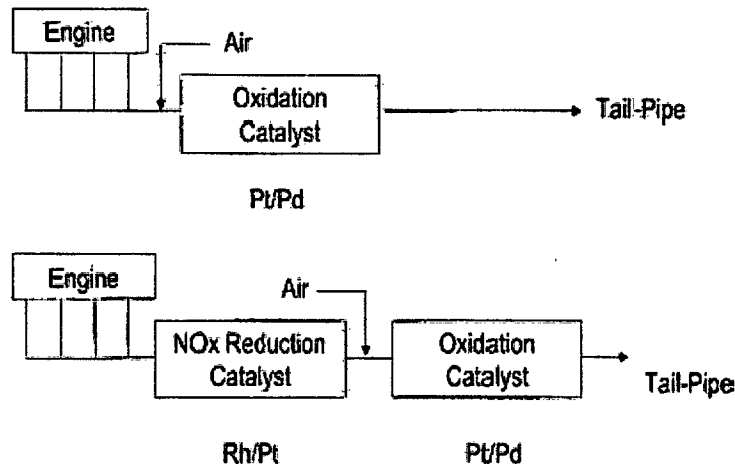
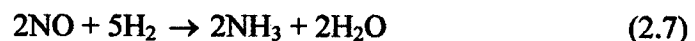


Figure 2.3 Schematic arrangement of oxidation catalyst and air injection point used initially to lower HC and CO emissions.

Nitric oxide is a thermodynamically unstable compound (enthalpy of formation $\Delta H_f = +90$ kJ/mol), it is a free radical yet under practical conditions in the presence of oxygen dissociation does not take place, and it can only be converted to nitrogen via a reductive process. The first approach for controlling NO_x from car engines was to reduce it over a platinum/rhodium catalyst in rich exhaust gas before air was added to permit oxidation of HC and CO over an oxidation catalyst. This arrangement and the earlier oxidation catalyst only system are illustrated schematically in figure 2.3. The selectivity of the catalyst used and the conditions employed for the NO_x reduction had to ensure a high degree of selectivity so as not to reduce NO_x to NH_3 or SO_2 to H_2S . These reactions shown in equation below are undesirable because of the smell and toxicity of the products.



Catalytic combustors have conventionally been modeled as a 'black box' that produces a desired amount of fuel conversion. The essential features predictions of the methane catalytic combustion; the monolith honeycomb catalytic reactor experiment by Bond *et al.* (1996) is simulated by a two-dimensional flow code with active catalyst surfaces. The computational domain contains two regions - a gas

phase reactor channel and a solid phase substrate wall. The energy conservation equation is solved for the solid wall so that the conductive heat transfer within the substrate can be properly determined. The predicted gas phase temperatures, methane percentage conversions, and carbon monoxide (CO) mole fractions are compared with the measurements by Bond et al. (1996).

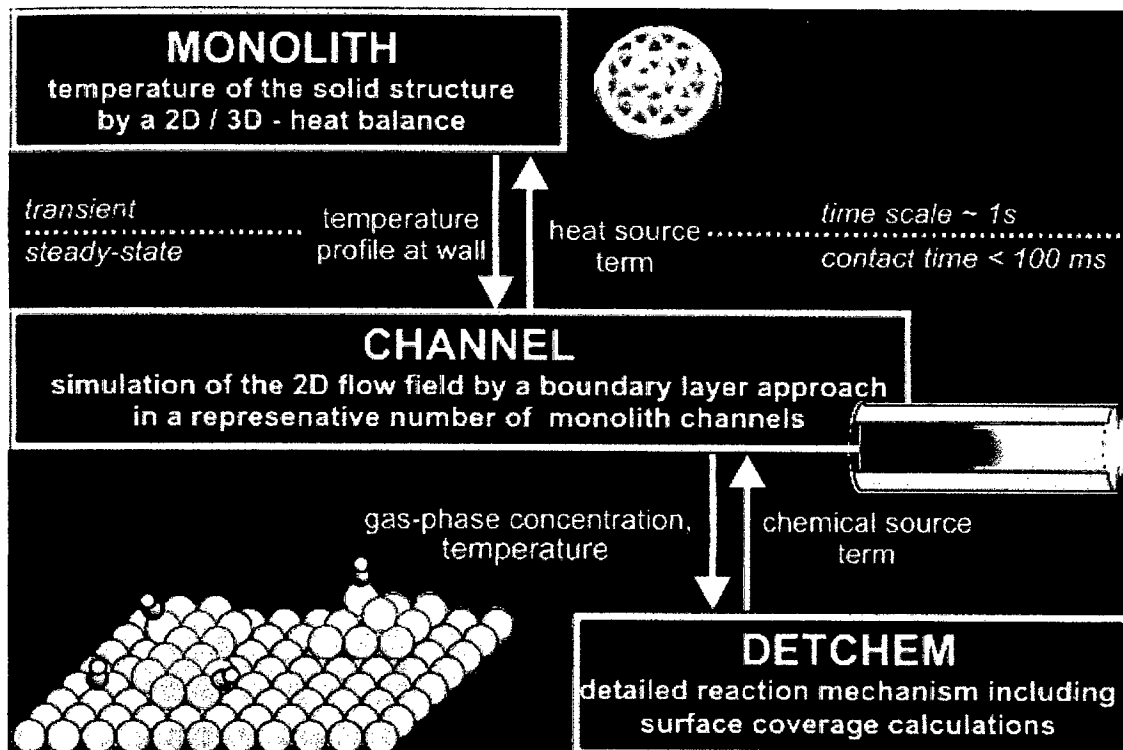


Figure 2.4 Catalytic combustion of methane on Pt

In a single channel of a monolith a variety of physical and chemical processes occur. The flow is laminar. The transport of momentum, energy and chemical species appear not only in axial but also in radial direction. The chemical species can react either in the gas phase or on the inner channel surface, which is coated with the catalyst. Diffusion is not only the diffusion between reactants to and products away from the wall but also species diffusion inside the pores of the catalyst surface, for example wash coat. The temperature distribution in the channel depends on convection, heat conduction in the gas phase and the solid channel wall, heat release by gas phase and surface reactions and thermal radiation

In the absence of external heat losses, average temperature and species profiles are more or less determined by the homogeneous reaction rates. And also, because at high steady-state operating temperature of the catalytic combustor, the heterogeneous reactions rates are well represented by the diffusion-controlled, fast wall limit.

Harrison and Ernst solved the equations for steady state heat and mass transfer in an adiabatic laminar turbulent flow reactor for the combustion of carbon monoxide. Three variations were investigated; homogenous-phase reactions only, heterogeneous reactions only or combined heterogeneous and homogenous reactions. Results of comparison from these models shows at high enough temperatures, homogenous gas phase reactions are unavoidable.

Bruno *et al* modeled the steady state combustion of propane in a monolith geometry using a two-dimensional steady-state fully developed laminar flow model. Heat transfer characteristics were included by using an experimental wall temperature profile in the model's gas-phase energy balance. Three overall reactions were used to model the homogeneous oxidation of propane along with infinitely fast (diffusion-controlled) heterogeneous kinetics. Trends of computed concentrations and temperature showed good qualitative agreement with experiments.

Griffin and Pfefferle (1990) studied gas phase and catalytic ignition of methane and ethane over platinum. They measured ignition temperatures of various mixture equivalence ratios and deduced the apparent activation energies at the surface ignition temperatures for both fuels. Their results show that the activation energy varies with the equivalence ratio, ϕ . The activation energy is about 188 kJ/mole for $\phi > 0.4$ and 88 kJ/mole for $0.2 < \phi < 0.4$. Since the surface ignition temperature varies with the equivalence ratio, the dependence of activation energy on equivalence ratio can be used to provide a relationship between activation energy and surface temperature. The activation energy plot for methane obtained by Griffin and Pfefferle also shows two kinetic regimes with a transition temperature *ca.* 870 K

corresponding to the surface ignition temperature for a mixture with $\phi = 0.4$. Because this mixture is lean, it is unlikely that CO would be the major species formed on the catalyst surface even at high temperatures. This change in activation energy might not be caused by the change in oxygen adsorption as seen in Trimm and Lam's experiments. Griffin and Pfefferle suggested that the higher activation energy at high surface temperatures may be the result of the greater reactivity of surface oxygen when its surface coverage is low.

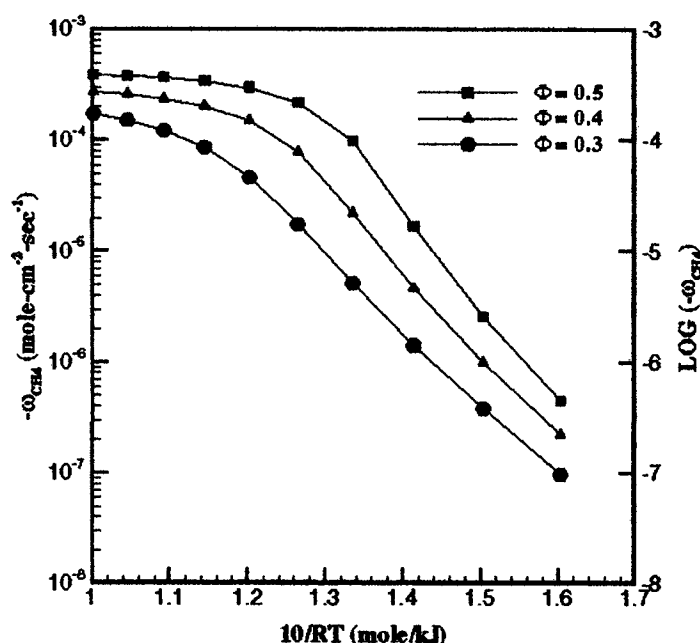


Figure 2.5 Arrhenius plots of the overall reaction rate predicted by the SPSR model for equivalence ratios of 0.3, 0.4, and 0.5

Figure 2.5 shows the Arrhenius plots of the overall reaction rate predicted by the SPSR model for equivalence ratios of 0.3, 0.4, and 0.5. The Arrhenius curves in Figure 2.5 show a smooth transition in the predicted activation energy from low values of 66-88 kJ/mole to high values of 166-212 kJ/mole. These apparent activation energies agree well with those determined by Griffin and Pfefferle (1990). The numerical model also predicts the transition of activation energy occurring at surface temperatures between 900 and 1000 K. Griffin and Pfefferle (1990), however, observed the transition in activation energy taking place at slightly lower

surface temperatures between 800 and 873 K. Curve-fittings of the Arrhenius relationship for CH₄-air mixture of equivalence ratio 0.4 are shown in Figure 2.6. The predicted apparent activation energy is seen to decrease from 186 kJ/mole to 77 kJ/mole when the surface temperature increases from 750 K to 1100 K. Note that the predicted overall activation energy by fitting the calculations over the entire temperature range is 136 kJ/mole which is close to the value used by the one-step surface reaction numerical model.

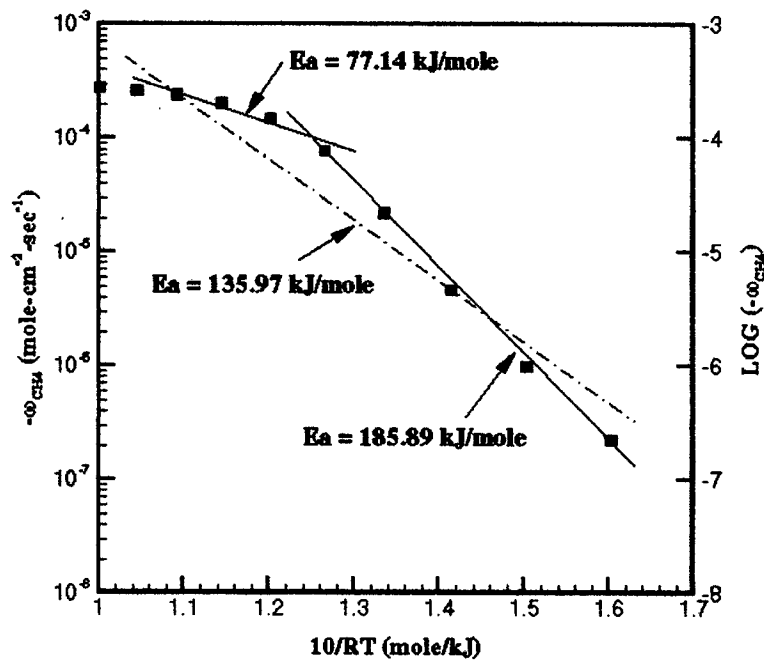


Figure 2.6 Arrhenius relationship for CH₄-air mixture of equivalence ratio 0.4

2.5 Wall surface reaction

Catalytic combustion includes several essential processes:

- 1) diffusion of the reactants from the gas phase to the catalytic surface
- 2) adsorption of the reactants onto the catalytic surface
- 3) movement of adsorbed species
- 4) reaction on the surface of the catalyst
- 5) desorption of the products from the surface
- 6) diffusion of the products from the catalytic surface to the gas phase

The adsorption process involves reactants being diffused from the gas mixture towards the catalyst surface, where molecules attach themselves onto surface. The surface reaction process occurs when the reactant molecules are attached. Product of these reactions are then released back into the gas mixture and diffused outwards.

2.5.1 Adsorption process

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term 'sorption' encompasses both processes, while desorption is the reverse process. There are two modes of adsorption of molecules (or adsorbates), onto the surface (or substrates) that is, one being physical adsorption or physisorption, and another one is being chemical adsorption or chemisorption. The main difference between these two modes is how the adsorbates are bonded to the substrates.

Table 2.1 Differences between chemisorption and physisorption

Mode	Chemisorption	Physisorption
Temperature Range	Virtually unlimited	Near or below the condensation point of the gas
Activation Energy of Adsorption	Rarely less than 80kJ/mol and often exceed 400kJ/mol	Typically in the range of 10 – 40kJ/mol
Nature of adsorption	Often dissociative and irreversible	Non-dissociative and reversible
Kinetics of adsorption	Varied – often an activated process	Fast – it is a non-activated process

2.5.2 Desorption process

In an indefinite state, the species attached on to surface may remain in that condition, as once, the species has absorbed enough thermal energy to compose three courses of actions. In the last course, it could free itself away from the surface and this action is known as the desorption process.