

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Background

Decarbonylation or dissociation of oxygenated compounds to liberate CO, H<sub>2</sub> and volatile or adsorbed hydrocarbons has been observed on a number of Group VIII metal catalysts. The detail of this chemistry will provide new insights into catalytic processes which are essentially its reverse e.g. higher oxygenate synthesis from CO and H<sub>2</sub>, which is important because of the increasing use of oxygenates including alcohol blends and MTBE as octane enhancers in gasoline. In addition, these results can contribute to better understanding of the catalytic oxidation of volatile organic compounds (VOCs). VOCs are commonly found to emit in dilute concentrations from many industrial processes and internal combustion engines. Control of VOC emissions is often accomplished by thermal incineration to CO<sub>2</sub> and H<sub>2</sub>O. Catalytic incineration can achieve conversions of greater than 99 % while operating at a lower temperature (673 to 773 K) than a thermal incinerator (973 to 1473 K). The reduced operating temperature also means less auxiliary fuel needed to preheat the waste stream and the incinerator. Also, the yield of oxygenates on ruthenium in Fischer-Tropsch synthesis is relatively low. Therefore, it is interesting to use ruthenium catalysts in the oxidation of oxygenated compounds.

There is a significant body of related works concerning Group VIII metal catalysts including gold and oxygenated compounds, and also including Fischer-Tropsch synthesis.

Brown and Barteau (1993) found that higher aliphatic aldehydes released CO plus alkyl groups via decarbonylation on Rhodium (Rh). Those alkyls were hydrogenated to volatile alkanes. They also concluded that higher alcohols were not dehydrogenated to form aldehydes and did not release volatile hydrocarbon products.

Yigong *et al.* (1993) studied the Fischer-Tropsch reaction on Ru/TiO<sub>2</sub> and Ru/SiO<sub>2</sub>. They showed that the catalytic chemistry occurred predominantly on Ru and that it was unaffected by the support.

Guczi (1988) concluded that the structure and catalytic activity of supported iron, cobalt, ruthenium, and nickel catalysts were significantly affected by the addition of a second metal. The suppression of inactive carbide in Fischer-Tropsch synthesis by addition of Ru or Ni to iron increased the catalytic activity and there was no oxygenate production. However, in the Pt-Ru/Al<sub>2</sub>O<sub>3</sub> system, some methanol or oxygenate formation was observed.

Abrevaya *et al.* (1988) pointed out that with alumina supported catalysts, the turnover frequency in Fischer-Tropsch synthesis increased with increasing the particle size of ruthenium metal. It was concluded that ruthenium was able to preserve its activity by preventing the buildup of carbonaceous deposits.

Solymosi *et al.* (1997) showed that dimethyl ether adsorbing on the supported Rhodium (Rh) was transformed into methoxy species at 200-300 K. The decomposition of ether molecules was catalyzed by Rhodium (Rh) above 473 K to give CO, H<sub>2</sub> and small amounts of hydrocarbon products. They concluded that the oxidation reaction proceeded through the activation of dimethyl ether by adsorbed O atoms and the transient formation of methoxy species on Rhodium (Rh). The kinetic order with respect to O<sub>2</sub> was found to be 0.4 and the order with respect to dimethyl ether was about 0.8.

Falconer and Cordi (1997) used the temperature-programmed desorption (TPD) and oxidation (TPO) to study decomposition and oxidation of methanol, ethanol, acetaldehyde, formic acid, and acetic acid on an Ag/Al<sub>2</sub>O<sub>3</sub> catalysts. It was found that methanol was decomposed by both dehydration and dehydrogenation to CO, H<sub>2</sub> at 600-900 K, dimethyl ether and H<sub>2</sub>O at lower temperature, small amount of CO<sub>2</sub> above 700 K, and the rest of methanol desorbed during 400-800 K.

Schwank and Datye (1985) reviewed a number of the applications of elemental gold in catalysis. It was reported that the activities of some gold-catalyzed oxygen transfer reactions for example, gold catalyzed the reduction of nitric oxide and the carbonyl group in acetone and the oxidative dehydrogenation of alcohols to aldehydes. Furthermore, there was an interest in supported gold catalysts for H<sub>2</sub> and CO oxidation at room temperature.

Lazaga and Wickham (1993) found that coadsorbed oxygen adatoms on the Au(111) surface could activate CH<sub>3</sub>OH dissociation to produce CO<sub>2</sub> and H<sub>2</sub>O. The methoxy species (CH<sub>3</sub>O) has been considered as an intermediate of the methanol decomposition. However, several transition metals surface can adsorb methanol molecule which can decompose to H<sub>2</sub> and CO.

Moreover, from the study conducted by Haruta *et al.* (1996), gold supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was as active as Al<sub>2</sub>O<sub>3</sub>-supported Pd and Pt catalysts in the oxidation of CH<sub>3</sub>OH, HCHO, and HCOOH. In addition, the gold catalysts were less active in H<sub>2</sub> oxidation but they were markedly more active in CO oxidation at low temperatures.

From all of the mentioned studies, it is very interesting to incorporate the group VIII and the group IB metal as bimetallic for oxidation of oxygenated compounds. Bimetallic catalysts are of considerable industrial significance because of their improved catalytic behaviors (activity,

selectivity, and poison resistance). Studies of supported bimetallic cluster catalysts are interesting subjects of fundamental catalytic investigations because it is likely to obtain any particular properties thought to influence chemisorptive and catalytic behavior simply by varying the relative content of the constituent metals. The term “bimetallic cluster”, coined by Sinfelt (1983), describes supported systems composing of metals that do not form bulk alloys. The bimetallic catalysts of Ru-Cu, Ru-Ag, and Ru-Au are examples of this type of catalyst where one of elements (Ru) is catalytically active for a variety of reactions and the second metal (Cu, Ag, or Au) is relatively inactive.

From the study of Galvagno *et al.* (1981), they studied the effect of different supports of Ru-Au catalysts on the ethane and propane hydrogenolysis. For Ru-Au/SiO<sub>2</sub>, the hydrogenolysis activity of ruthenium decreased by two orders of magnitude with addition of gold. It was suggested that ruthenium and gold did not exist as separate particles but formed bimetallic aggregates. The results obtained from chemisorption and XPS experiments showed a surface composition similar to the bulk. This was different from Ru-Au/MgO systems on which an enrichment of ruthenium on the surface of bimetallic Ru-Au clusters was discovered. It was concluded that the strength of metal-support interaction can affect the surface composition of multimetallic supported systems.

Datye *et al.* (1984) modeled this bimetallic as Ru particles with Au adsorbed on the surface. They characterized the morphology of these catalysts and classified them into three size ranges (less than 4 nm, 4-15 nm, and more than 15 nm) and numerous particles within a given size range were analyzed.

Schwank and Datye (1985) observed a clear bimodal particle size distribution of the bimetallic Ru-Au supported on silica. All the large particles were monometallic Au particles. These large Au particles seemed to be very weakly attached to the SiO<sub>2</sub> support, leading to a greater mobility of Au. The reduction of both metals seemed to occur simultaneously allowing bimetallic

cluster formation. This was contrasted with Ru-Au/MgO, which was phase-segregated, pseudo-bimetallic, and did not represent true bimetallic. They also reported the results of the silica-support Ru-Au system that showed a monotonic decline in turnover frequency with increasing gold content and decreasing ruthenium content. No change was reported for activation energies with varying gold contents, suggesting perhaps that gold served to dilute active ruthenium ensembles. Slight shifts in product distributions to larger molecules occurred when the ratio of gold to ruthenium was increased.

In addition, Tauszik *et al.* (1984) found the metal-metal and metal-support interactions in Ru-Au catalysts supported on MgO and SiO<sub>2</sub>. These interactions modified the nature of the species formed after impregnation and drying, and the oxidizability after reduction.

As mentioned earlier, ruthenium catalysts have been found wide application as hydrogen and oxygen transfer catalysts. It has been widely known about the ability of ruthenium to activate oxygen and the unusual activity of supported gold for oxygen transfer reactions, and so it is very interesting to investigate the oxygen transfer abilities of supported ruthenium-gold catalysts. Moreover, at the University of Michigan, it has been carried out a number of studies on ruthenium and bimetallic ruthenium-gold catalysts for reactions such as hydrocarbon hydrogenolysis and CO hydrogenation (Fischer-Tropsch synthesis). The purpose of introduction of bimetallic catalysts is to modify the properties of catalyst samples to be active for the catalytic reaction at lower temperatures.

A series of ruthenium and ruthenium-gold catalysts with varying gold content have already been synthesized at the University of Michigan and characterized by hydrogen adsorption, electron microscopy and photoelectron spectroscopy as they are described above.

## **2.2 Theory**

### **2.2.1 Temperature-Programmed Methods**

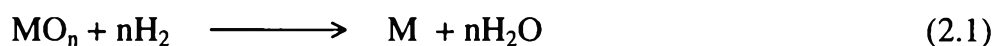
The basic idea of these methods is to monitor surface or bulk reactions of solid catalysts with their gaseous environment by performing a continuous analysis of the gas phase. Temperature-programmed methods form a class of techniques in which a chemical reaction is monitored while the temperature increases linearly with time. Several techniques are in use (i.e. temperature-programmed reduction (TPR), temperature-programmed desorption (TPD), temperature-programmed oxidation (TPO), temperature-programmed sulfidation (TPS), and temperature-programmed reaction spectroscopy (TPRS)). All these techniques are applicable to real catalysts and single crystals and have several advantages that they are experimentally simple and inexpensive in comparison to many other spectroscopies. Interpretation on a qualitative basis is simply straightforward. However, obtaining reaction parameters such as activation energies or pre-exponential factors from temperature-programmed methods is rather complicated (Niemantsverdriet, 1993).

#### **(a) Temperature-Programmed Reduction (TPR)**

Temperature-programmed reduction (TPR) was first proposed by Robertson and coworkers in 1975 (Delannay, 1984). TPR is used to determine the number of reducible species present in the catalyst and can reveal the temperature at which the reduction occurs. An important aspect of TPR analyses is that the sample does not need to have any special characteristics other than containing reducible metals.

The TPR analysis begins by flowing hydrogen in an inert carrier gas such as nitrogen or argon over the sample, usually at ambient temperature. While the gas is flowing, the temperature of the sample is increased linearly with time and the consumption of hydrogen by adsorption/reaction is monitored. Changes in the concentration of the gas mixture are determined. This information directly yields the hydrogen uptake volume (Niemantsverdriet, 1993).

Reduction is an inevitable step in the preparation of metallic catalysts. It is also a critical step because if it is not done right, the catalyst may sinter or may not reach its optimum state of reduction. The reduction of a metal oxide,  $MO_n$  by  $H_2$  is described by equation (2.1):



Thermodynamically, the reduction will proceed when the change in Gibbs free energy,  $\Delta G$ , has a negative value. The following expression shows how  $\Delta G$  depends on pressure and temperature:

$$\Delta G = \Delta G^0 + nRT \ln \frac{p_{H_2O}}{p_{H_2}} \quad (2.2)$$

where

$\Delta G$  is the change in Gibbs free energy for the reduction

$\Delta G^0$  is the same under standard conditions

$n$  is the stoichiometric coefficient of reaction

$R$  is the gas constant

$T$  is the temperature

$p$  is the pressure.

If a catalyst sample is reduced under flowing hydrogen, the reaction product water is removed effectively and the second term in equation (2.2) is

therefore always negative. For many oxides, such as those of cobalt, nickel and the noble metals,  $\Delta G^0$  is already negative and reduction is thermodynamically feasible. All one has to do is find a temperature where the kinetics is rapid enough to achieve complete reduction (Niemantsverdriet, 1993).

In general, TPR measurements are interpreted on a qualitative basis. In a supported catalyst, all particles should have the same morphology and all atoms of the supported phase should be affected by the support in the same way, otherwise the TPR pattern would represent a combination of different reduction reactions. Such strict conditions are seldom obeyed in supported catalysts but are more easily met in unsupported particles (Delannay, 1984).

TPR is a highly useful technique to provide a quick characterization of metallic catalysts. It gives information on the phases present after impregnation and on the eventual degree of reduction. For bimetallic catalysts, TPR patterns often indicate if the two components are mixed or not. In favorable cases where the catalyst particles are uniform, TPR yields activation energies for the reduction, as well as mechanistic information.

### **(b) Temperature-Programmed Desorption(TPD)**

Temperature-programmed desorption (TPD) was developed in 1963 by Amenomiya and Cvetanovic (Delannay, 1984). It is a common way to explore the influence of adsorbate phase behavior on the kinetics of surface process. It determines the number, type, and strength of active sites available on the surface of a catalyst from measurement of the amount of gas desorbed at various temperatures.

After the sample has been outgassed, reduced, or otherwise prepared, a gas or a mixture of interesting gases flows over the sample and is adsorbed onto the sample at ambient temperature. The sample is then heated in such a



way that the temperature varies linearly with time while a steady stream of inert carrier gas flows over the sample. Typically, some of the reaction products desorb from the surface. In a TPD experiment a mass spectrometer is used to monitor the desorption of products. The result is so-called TPD spectrum that is a plot of the desorption rate of products as a function of the sample temperature. In a TPD spectrum, there are a series of peaks corresponding to desorption of the reaction products. Each of peaks in the TPD spectrum represents a different kinetic process. Generally, processes having a lower activation barrier will have a lower peak temperature in TPD in comparison to the processes having a higher barrier. Basically, if a process has a high reaction barrier, one needs to go to a high temperature to obtain the peak of desorption. Unfortunately, it cannot really tell much about what the kinetic processes are like from its TPD spectrum. There will be multiple peaks in TPD as though there are different “states” of the adsorbate on the surface accounting for each kinetic process seen in TPD. For example, if there are four different binding sites for the adsorbate, it is expected the desorption from each binding site to be different. As a result, there will be multiple desorption pathways and therefore multiple peaks in TPD.

At a certain temperature, the heat will overcome the activation energy. Therefore, the bond between the adsorbate and adsorbent will break and the adsorbed species will desorb. Under the presence of different active metals, they usually desorb the reacted species at different temperatures. These desorbed molecules enter the stream of inert carrier gas and are swept to the detector which measures the gas concentrations. The volume of desorbed species combined with the stoichiometry factor, and the temperature at which pre-adsorbed species desorb, yields the number and strength of active sites.

### 2.2.2 Bimetallic Catalysts

Scientists have been interested in bimetallic systems as catalysts for many years. For a decade or longer beginning shortly after World War II, most attention was devoted to the use of metal alloys as catalysts to probe the relationship between the catalytic activity of a metal and its electronic structure. One type of alloy which has been investigated extensively is consisted of a group VIII and a group IB metals.

According to energy band theory of electrons in metals, transition metals such as those of group VIII possess d-bands whose states are not completely occupied by electrons. By contrast, the d-band of nontransition metals such as those of group IB are completely filled (Table 2.1). The substitution of a group IB for a group VIII in the metal lattice adds electrons to the system. The holes in the d-band of transition metals could be filled and as

**Table 2.1 The electron structure of the transition metal group VIII and non-transition metal group IB (Perry *et al.*, 1984)**

<b>Group VIII</b>	<b>Group IB</b>
Fe : [Ar]3d <sup>6</sup> 4s <sup>2</sup>	Cu : [Ar]3d <sup>10</sup> 4s <sup>1</sup>
Ru : [Kr]4d <sup>7</sup> 5s <sup>1</sup>	Ag : [Kr]4d <sup>10</sup> 5s <sup>1</sup>
Os : [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	Au : [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
Co : [Ar]3d <sup>7</sup> 4s <sup>2</sup>	
Rh : [Kr]4d <sup>8</sup> 5s <sup>1</sup>	
Ir : [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	
Ni : [Ar]3d <sup>8</sup> 4s <sup>2</sup>	
Pd : [Kr]4d <sup>10</sup> 5s <sup>0</sup>	
Pt : [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	

a consequence the chemisorption and adsorption would be considerably influenced. The alloys possess d-bands with fewer unoccupied states than pure group VIII metal does. In this view, an alloy possesses a single d-band rather than separate bands for two components and the additional electrons introduced with a group IB would lead to an alloy with a more completely filled d-band. To test the hypothesis that the catalytic activity of a group VIII metal is associated with an unfilled d-band, many attempts were carried out to determine reaction rates on alloys such as nickel-copper and palladium-gold as a function of composition (Sinfelt, 1983). It is believed that the extent of filling of d-band would be determined by the composition of the alloy; hence it should be possible to relate catalytic activity to d-band vacancies.

With the present status of our knowledge about bimetallic catalysis, it can be briefly summarized as follows (Bradky *et al.*, 1989):

(a) The composition of the equilibrated alloys surface can differ substantially from that of the bulk, and chemisorption or the catalytic reaction itself can induce additional changes in the surface composition.

(b) The selectivity patterns are mainly determined by the ensemble size effect, but a ligand effect may also occur simultaneously. It is now generally accepted that the individual surface atoms retain their character in alloys, and their catalytic properties are mainly determined by their nearest neighbors. If more than one catalytically active metal atom is required to create an active site for the reaction, the system is said to display an ensemble effect. The rate of reaction will fall off faster than the surface composition decreases.

(c) Alloys often exhibit higher catalytic activity than either of their constituents because of a lower degree of poisoning. This can result in higher catalyst stability and selectivity for a given reaction. Typically, hydrogenolysis is suppressed by alloying, while hydrogenation and isomerization are not significantly affected.

There are two main resources interests of bimetallic catalyts (Sinfelt, 1963):

(a) The investigation of selectivity effects in catalysis by such bimetallic materials.

(b) The preparation and characterization of highly dispersed bimetallic catalyts.

Two types of bimetallic catalyts are generally classified according to their catalytic reaction. The first type of a combination of atoms of a group VIII metal and a group IB metal, and the other consists of two different atoms of metal in the same group VIII metals. It has been discovered that the activity of the group VIII metal for hydrogenolysis reactions of hydrocarbons decreases markedly by the presence of the Group IB metal. It has been shown that the inhibition of hydrogenolysis leads to improved selectivity for alkane isomerization reactions and for reactions in which saturated hydrocarbons are converted to aromatic hydrocarbons (Sinfelt *et al.*, 1972).

Bimetallic systems of interest are not limited to combinations of metallic elements that are highly miscible in the bulk. For example, the ruthenium-copper system, in which the two components are virtually completely immiscible in the bulk, exhibits selective inhibition of hydrogenolysis similar to that observed with the nickel-copper system. The latter, of course, is well known as a system in which the two components form a complete series of solid solutions (Sinfelt, 1983).

Since the ability to form bulk alloys is not of interest as a catalyst and so it is decided not to use the term "alloy" in referring to bimetallic catalyts, in general. Instead, terms such as bimetallic aggregates or bimetallic clusters have been adopted in preference to alloys. In particular, bimetallic clusters refer to bimetallic entities which are highly dispersed on the surface of a carrier. For a system such as ruthenium-copper, it appears that the two components can interact strongly at an interface, despite the fact that they do

not form solid solutions(alloys) in the bulk. In this system, the copper is present at the surface of the ruthenium, much like a chemisorbed species (Sinfelt, 1983).

### 2.2.2.1 Ruthenium-Gold Catalysts

Among the group VIII metals, Ru occupies an intermediate position between Fe, Co, Ni and noble metals, regarding to the metal-oxygen interactions (see Table 2.2). Supported Ru-Au catalysts have attracted attention for several reasons. These metals are almost immiscible in the bulk state, so it appeared of interest to inquire into possibility of their interaction in the dispersed state. Furthermore, gold catalysts can display an activity comparable to that of platinum and the metal-support interactions are found in both gold and ruthenium monometallic catalysts.

**Table 2.2 Metal-Oxygen Interaction for Pt, Ru, and Ni (Koopman *et al.*, 1981)**

	Pt	Ru	Ni
Heat of formation of oxide (kJ/mol)	-134	-220	-243
Heat of chemisorption of oxygen (kJ/mol)	-109	-176	-235
Reduction temperature (K)	293	433	573

Ruthenium has wide application as hydrogen and oxygen transfer catalysts. It has been known about the high ability of ruthenium to activate

oxygen and the unusual activity of supported gold for oxygen transfer reactions and so it is very interesting to investigate the oxygen transfer abilities of supported ruthenium-gold catalysts. Ruthenium also gives the low yield of oxygenates in Fischer-Tropsch synthesis comparing to the other metal catalysts (Schwank and Datye, 1985).

The addition of Au to Ru, mainly studied by the Ann Arbor group (Datye *et al*, 1984), is a rather interesting attempt to influence the catalytic activity of Ru. According to these studies, the support exerts a stabilization effect on the bimetallic cluster. That is, on silica support, a bimodal particle-size distribution was detected because Au tended to aggregate in the form of large particles, whereas Ru remained in a highly dispersed state (whether the latter contains Au or not is still an open question). On the other hand, on MgO, evidence was found for the existence of bimetallic Ru-Au particles with a diameter of 10 nm.

It seems more difficult to interpret other catalytic behaviour of the SiO<sub>2</sub> and MgO supported Ru-Au catalysts. On Ru-Au/SiO<sub>2</sub>, the addition of Au decreases the catalytic activity in ethane hydrogenolysis and in the CO + H<sub>2</sub> reaction, while MgO-supported catalysts show a maximum in activity with the addition of Au. According to the authors, this might be due to an electronic effect of alloying the two metals. However, with the experimental data available we can also speculate that the effect of Au is simply an ensemble size effect in the self-poisoning reaction. As was shown with silica, small particles of Ru are present and are subjected to carbon deposition, which partially deactivates the active ruthenium component and the catalytic activity thus decreases. On the other hand, the existence of bimetallic particles has been demonstrated on MgO-supported catalysts. Thus the addition of Au probably decreases the ruthenium ensemble size and consequently also self-poisoning reactions leading to deactivation. At the higher level of Au, too much of the total catalyst surface becomes covered by Au, leading to a decrease in the overall

activity. This interpretation is supported by the fact that the behavior of the catalyst in both reactions is the same, although their mechanism are completely different. The data presented seem to be explained satisfactorily by the effects of the support, the ensemble size and the suppression of side reactions.

It has been widely known that Ru-Ag, and Ru-Cu bimetallic catalysts are relatively simple and easy to study (Narayan and King, 1998). One of the advantages of these model systems is that at low concentrations the group IB element preferentially occupies the edges, corners, and other low coordination metal sites on the catalyst surface (Strohl and King, 1989). This preferential segregation of Ag and Cu to the low metal coordination sites on the surface of the bimetallic catalyst can be used to manipulate the surface structure and its influence on activity and selectivity. In addition, the studies of hydrogenolysis and CO hydrogenation can provide insight regarding the surface composition of the catalytic site responsible for their activity (Smale and King, 1990).

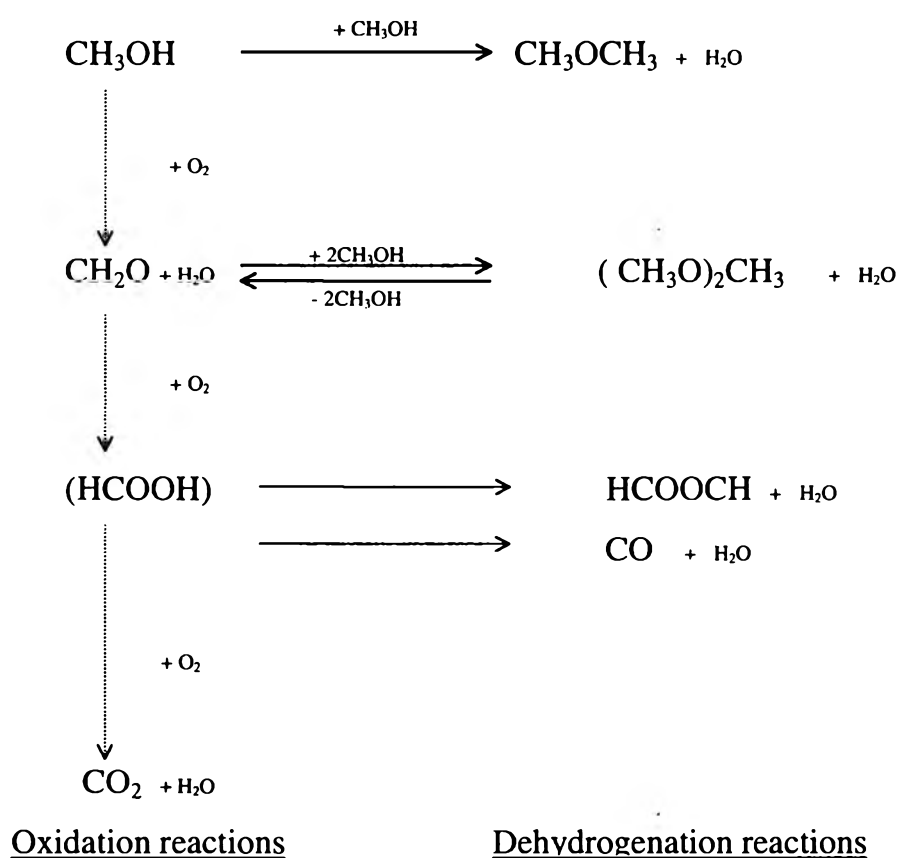
### **2.2.3 Methanol Oxidation**

The methanol oxidation can lead to various products depending on the catalyst, reaction temperature, and reactant partial pressure. The main reaction product cited in the literature is formaldehyde ( $\text{CH}_2\text{O}$ ), because of its industrial interest. However, it is also reported that significant amounts of dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ), methyl formate ( $\text{HCOOCH}_3$ ), methylal ( $(\text{CH}_3\text{O}_2\text{CH}_2)$ ) and carbon oxides can be formed during methanol oxidation. Surprisingly, the formation of formic acid ( $\text{HCOOH}$ ) is rarely observed. This product is considered as an intermediate in the formation of methyl formate or carbon oxides. The formation of hydrogen is never observed when oxygen containing feed is used; only water is detected (Tatibouët, 1997).

Tatibouët (1997) showed the different pathways of methanol oxidation as shown in Figure 2.1. These reactions can be divided into two principal pathways:

(i) reactions of oxidations which need oxygen (molecular or supplied by the catalyst).

(ii) reactions of dehydrogenations which do not need oxygen.



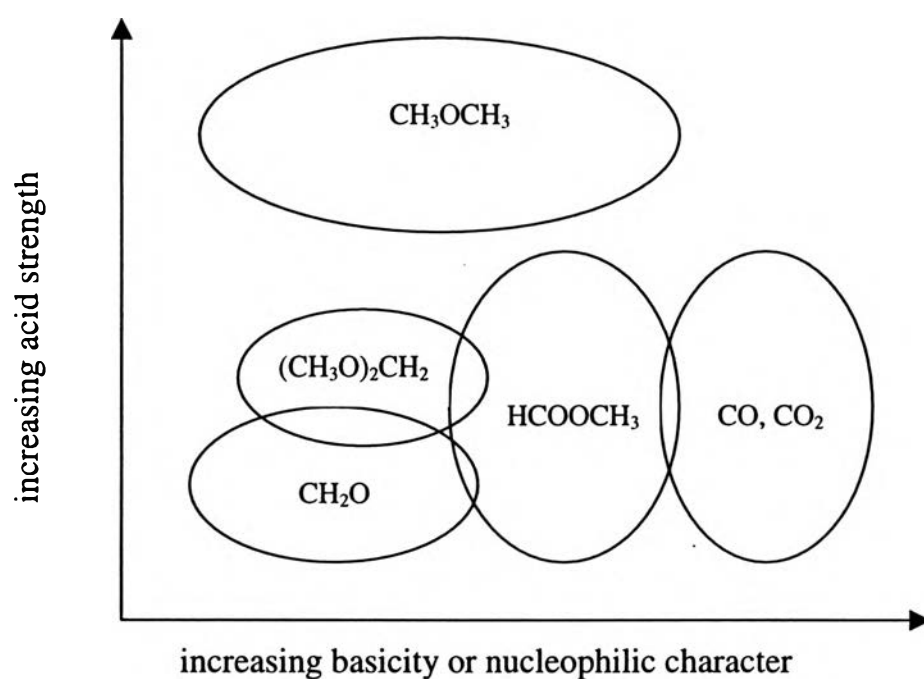
**Figure 2.1 Pathway of methanol oxidation (Tatibouët, 1997)**

According to this pathway, except for dimethyl ether, which is obtained directly by a bimolecular dehydration of methanol, the formation of all the products needs at least one oxidation step.

The formation of these different products can be summarized in an acid-strength diagram (Figure 2.2). Three main zones can be distinguished,



which roughly correspond to the formation of dimethyl ether (high acidic character), carbon oxides (high basic character) and mild oxidation products (bi-functional acid-base character).



**Figure 2.2 Schematic representation of the main reaction products as a function of the acido-basic character of the active sites (Tatibouët, 1997)**