CATALYTIC CONVERSION OF METHANE AND CARBON DIOXIDE IN CONVENTIONAL FIXED BED AND DIELECTRIC BARRIER DISCHARGE PLASMA REACTORS

ISTADI

UNIVERSITI TEKNOLOGI MALAYSIA
CATALYTIC CONVERSION OF METHANE AND CARBON DIOXIDE IN
CONVENTIONAL FIXED BED AND DIELECTRIC BARRIER DISCHARGE
PLASMA REACTORS

ISTADI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
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Specially dedicated to my beloved mother and father, 
my beloved wife Warti Istadi, my daughter Aisyah Muthmainah Istadi, 
and my beloved son Ridwan Firdaus Istadi
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ABSTRACT

The natural gases in the Natuna and Arun fields have CO$_2$/CH$_4$ ratio being 71/28 and 15/75, respectively. These ratios are potential for the production of C$_2$+ hydrocarbons and synthesis gas. The purpose of this study is to develop a new catalytic process for CH$_4$ and CO$_2$ utilization to produce C$_2$ hydrocarbons and/or synthesis gas at high conversion and selectivity. The studies started with a thermodynamic equilibrium analysis of CH$_4$ and CO$_2$ reactions to produce C$_2$ hydrocarbons and synthesis gas in order to investigate the feasibility of the reactions thermodynamically. The results showed that carbon dioxide reforming of methane, reverse water gas shift reaction, and dehydrogenation of ethane to ethylene were more viable than CO$_2$ oxidative coupling of methane. In the catalytic system, CeO$_2$-based catalyst screening was performed. The CaO-MnO/CeO$_2$ catalyst system displayed high stability suitable for the CO$_2$ oxidative coupling of methane. Moreover, the operating parameters, such as the CO$_2$/CH$_4$ feed ratio and reactor temperature, and the catalyst compositions, such as wt% CaO and wt% MnO, were optimized by using Weighted Sum of Squared Objective Functions algorithm. The synergistic effect of basicity and reducibility towards the catalytic activity were also addressed using XRD, CO$_2$-TPD and H$_2$-TPR. The synergistic effect of catalyst basicity and reducibility are vital in enhancing the reaction performance. Since the conversion and yield were still low, the conventional CO$_2$ oxidative coupling of methane was replaced with a more advanced reactor. The hybrid catalytic dielectric-barrier discharge plasma reactor was utilized for the synthesis gas and C$_2$+ hydrocarbons (ethane, ethylene, acetylene, and propane) production in one step. The new reactor system displayed promising performance at low temperature over CaO-MnO/CeO$_2$ catalyst. Next, a hybrid Artificial Neural Network – Genetic Algorithm technique was used to facilitate modelling and optimization of the plasma reactor system for both non-catalytic and catalytic dielectric barrier discharge plasma reactors. It was found that the catalytic dielectric barrier discharge plasma reactor performed better performance than the non-catalytic one and the conventional fixed bed reactor. The main products from the plasma reactor were ethane, carbon monoxide, propane, and hydrogen, while the minor products were ethylene and acetylene.
ABSTRAK

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### LIST OF ABBREVIATIONS

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<th>Description</th>
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<tr>
<td>O$_2$ OCM</td>
<td>Oxygen Oxidative Coupling of Methane</td>
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<td>CO$_2$ OCM</td>
<td>Carbon Dioxide Oxidative Coupling of Methane</td>
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<tr>
<td>syngas</td>
<td>Synthesis Gas</td>
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<tr>
<td>CORM</td>
<td>Carbon Dioxide Reforming of Methane</td>
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<td>RWGS</td>
<td>Reverse Water Gas Shift</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<td>FT-IR</td>
<td>Fourier Transform Infra Red</td>
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<td>CO$_2$-TPD</td>
<td>CO$_2$ Temperature Programmed Desorption</td>
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<td>H$_2$-TPR</td>
<td>H$_2$ Temperature Programmed Reduction</td>
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<td>DBD</td>
<td>Dielectric Barrier Discharge</td>
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<td>WSSOF</td>
<td>Weighted Sum of Squared Objective Function</td>
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<td>ANN</td>
<td>Artificial Neural Network</td>
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<td>GA</td>
<td>Genetic Algorithm</td>
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<td>CCD</td>
<td>Central Composite Design</td>
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<td>RSM</td>
<td>Response Surface Methodology</td>
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<td>S</td>
<td>Catalyst Support</td>
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<td>M$_1$O</td>
<td>First metal oxide in ternary metal oxide</td>
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<td>M$_2$O</td>
<td>Second metal oxide in ternary metal oxide</td>
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<td>M$_3$O</td>
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<td>TCD</td>
<td>Thermal Conductivity Detector</td>
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<td>PRSS</td>
<td>Petronas Research &amp; Scientific Services</td>
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<td>HP</td>
<td>Hewlet Packard</td>
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<td>GC</td>
<td>Gas Chromatography</td>
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<td>RT</td>
<td>Retention Time</td>
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<td>MTG</td>
<td>Methanol to Gasoline</td>
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<td>NSGA</td>
<td>Non-dominated Sorting Genetic Algorithm</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>CCRD</td>
<td>Central Composite Rotatable Design</td>
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<td>ANOVA</td>
<td>Analysis of Variance</td>
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<td>GHSV</td>
<td>Gas Hourly Space Velocity</td>
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<td>MLP</td>
<td>Multi-Layered Perceptron</td>
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<td>MSE</td>
<td>Mean Square Error</td>
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<td>MIMO</td>
<td>Multi Input and Multi Output</td>
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**LIST OF SYMBOLS**

- $b$ - Instrument peak broadening
- $b$ - Network bias parameters for hidden and output layers of the network
- $b^H$ - Scalar bias corresponding to hidden layer
- $b_j$ - Total population in moles of the $j$th atom in the system
- $b^O$ - Scalar bias corresponding to output layer
- $C$ - Dielectric capacity
- $d$ - Distance between parallel-plate electrodes
- $\hat{F}_i$ - Normalized response/objective function $i$
- $\hat{f}_i$ - Fugacity of species $i$ in solution
- $f_i^o$ - Fugacity of pure species $i$ in its standard state
- $F \in \mathcal{R}^M$ - Mapped objectives function space
- $F(X)$ - Multi-response objectives function
- $f(X)$ - Single-response objective function
- $f_1, f_2$ - Nonlinear activation/transfer functions
- $F_i$ - Inverted objective functions for minimization problem
- $F_{i,o}$ - Real objective functions for minimization problem
- $\bar{g}_i$ - Partial molar Gibbs free energy of the $i$th species in solution
- $g_i^o$ - Gibbs free energy of the pure $i$th species at standard conditions
- $\Delta G_i^o$ - Standard Gibbs free energy changes at temperature $T$
- $\Delta H_i^o$ - Heat of reaction at reference temperature
- $\Delta G_0^o$ - Gibbs free energy changes at reference temperature
- $\Delta C_p^o$ - Standard heat capacity change of reaction
- $G$ - Total Gibbs free energy
Gen - Generation index
Gen_{max} - Maximum generation in Genetic Algorithm
G_i(X) - \( i \)th equality constraints
H_j(X) - \( j \)th inequality constraints
I - Electric current
K - Equilibrium constant
k - Number of factor
MSE - Mean-Squared Error
n - Order of the reflection
N - Total number of moles in the reaction mixture
n_c - Number of points in the cube portion of central composite design
N_i - Mole of each chemical species \( i \)
n_{ji} - Number of the \( j \)th atoms that appear in the \( i \)th molecule
N_p - Number of patterns node used in the training
N_{pop} - Number of population
nvars - Number of independent variables in Genetic Algorithm
P - System pressure
P - Electric power
P_{cross} - Crossover fraction
P_0 - Standard pressure
Q - Charge
R - Universal gas constant
R^2 - Determination coefficient
S - Area of electrode
S(i) - Selectivity of species \( i \)
T - System temperature
t - Time
T_0 - Reference temperature
\( t_{i,k} \) - Desired (target) value of the \( k \)th output node at \( i \)th input pattern
V - Input voltage
W - Weighted input
W - Network weight parameters for hidden and output layers of the network
\( W^{HI} \) - Weights between input and hidden nodes
\( w_i \) - Weighting factor of objective function \( i \)
\( W^O \) - Weights between hidden and output nodes
\( X \in \mathbb{R}^N \) - Parameter space
\( X(i) \) - Conversion of species \( i \)
\( x^* \) - Optimized population or decision variable vector
\( X_i, x_i \) - Uncoded and coded independent variables, respectively
\( Y(i) \) - Yield of species \( i \)
\( y^H \) - Outputs vector from hidden layer
\( y_i \) - Mole fraction of the \( i \)th species
\( y_{i,k} \) - Predicted values of the \( k \)th output node at \( i \)th input pattern
\( y^O \) - Outputs vector from output layer
\( \alpha \) - Star point in central composite design
\( \beta_0 \) - Intercept coefficient in RSM model
\( \beta_j \) - Linear terms in RSM model
\( \beta_{ij} \) - Squared terms in RSM model
\( \beta_{ij} \) - Interaction terms in RSM model
\( \varepsilon \) - Permittivity of dielectric
\( \Sigma \) - Summation of data
\( \lambda \) - Wavelength of the X-radiation (=0.154 nm)
\( \hat{\phi}_i \) - Fugacity coefficient of the \( i \)th species in solution
\( \Omega \) - Feasible region
\( \Lambda \) - Mapped feasible region
\( \theta \) - Diffraction angle
\( \nu \) - Stoichiometric number of reaction
\( \nu_i \) - Stoichiometric coefficient of species \( i \) in reaction
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CHAPTER 1

INTRODUCTION

1.1 Methane and Carbon Dioxide Utilization

Natural gas is an abundant fossil fuel resource found all over the world. Though amounts of other gases, such as ethane, propane, H₂S and CO₂, may be present, methane (CH₄) is the main component of the natural gas. The composition of the natural gas is dependent on the location from where it is produced as listed in Table 1.1. Carbon dioxide (CO₂) is one of the most important greenhouse gases. Mitigation of CO₂ emission from various sources has been a worldwide objective. The emission contains particularly about 83% of carbon dioxide, 9% of methane, 6% of nitrous oxide and 2% of hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride (Song, 2001). It has been recognized that enhanced capacities in the area of chemical catalysis could have a significant role in addressing the global atmospheric CO₂ problem. The utilization of CO₂ gas to produce more valuable chemicals is very attractive.

Most of natural gases are located in remote areas, which require a proper infrastructure to transport the gas. As shown in Table 1.1, Malaysia has about 85.8 trillion standard cubic feet of natural gas and ranks as the 11th world’s largest natural gas reserve (Sarmidi et al., 2001). Therefore, on-site conversion of natural gas into higher valuable products brings out the advantages economically. Another resources as presented in Table 1.2 natural gas from Natuna’s and Arun’s fields in Indonesia contains CO₂ and CH₄ with CO₂/CH₄ ratio of 71/28 and 15/75, respectively ((Suhartanto et al., 2001; Centi et al., 2001). The highly CO₂/CH₄ ratio is potential
to produce higher hydrocarbon, oxygenates and more valuable chemical. A new technology for utilization of carbon dioxide and methane gases is very challenging.

Table 1.1: Gas reserves in Malaysia (Ministry of Energy, Communication, and Multimedia Malaysia, 1999)

<table>
<thead>
<tr>
<th>Region</th>
<th>Trillion standard cubic feet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peninsular Malaysia</td>
<td>34.4</td>
</tr>
<tr>
<td>Sabah</td>
<td>43.7</td>
</tr>
<tr>
<td>Sarawak</td>
<td>7.7</td>
</tr>
<tr>
<td>Total</td>
<td>85.8</td>
</tr>
</tbody>
</table>

Table 1.2: Composition of natural gas (in % vol.) from various locations

<table>
<thead>
<tr>
<th>Component</th>
<th>Terengganu (Malaysia) 1)</th>
<th>Natuna (Indonesia) 2)</th>
<th>Terrell County (Texas USA) 3)</th>
<th>Arun (Indonesia) 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH\textsubscript{4})</td>
<td>80.93</td>
<td>28.0\textsuperscript{a}</td>
<td>45.7</td>
<td>75</td>
</tr>
<tr>
<td>Ethane (C\textsubscript{2}H\textsubscript{6})</td>
<td>5.54</td>
<td>-</td>
<td>0.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Propane (C\textsubscript{3}H\textsubscript{8})</td>
<td>2.96</td>
<td>-</td>
<td>-</td>
<td>3.4\textsuperscript{b}</td>
</tr>
<tr>
<td>Butane (C\textsubscript{4}H\textsubscript{10})</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\geq C_5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Nitrogen (N\textsubscript{2})</td>
<td>0.10</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Carbon dioxide (CO\textsubscript{2})</td>
<td>8.48</td>
<td>71.0</td>
<td>53.9</td>
<td>15</td>
</tr>
<tr>
<td>Hydrogen Sulfida (H\textsubscript{2}S)</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\textsuperscript{a} CH\textsubscript{4} + low C\textsubscript{2}+ hydrocarbons
\textsuperscript{b} C\textsubscript{3}, C\textsubscript{4} hydrocarbons
1) Gordon et al. (2001)
2) Suhartanto et al. (2001)
3) Bitter (1997)
4) Centi et al. (2001)

Conversion of methane and carbon dioxide is important subject in the field of C\textsubscript{1} chemistry. Several technologies have been proposed to improve the efficiency of energy conversion and utilization of CO\textsubscript{2}. Alternatively, the recovered CO\textsubscript{2} can be used to produce high value-added chemicals, fuels and other useful products. There are several motivations for producing chemicals from CO\textsubscript{2} whenever possible: (1) CO\textsubscript{2} is an inexpensive, non-toxic feedstock, (2) CO\textsubscript{2} is a renewable feedstock compared to oil or coal, (3) the production of chemicals from CO\textsubscript{2} can lead to new
materials such as polymers, (4) new routes to existing chemical intermediates and products could be more efficient and economical than existing method, (5) The production of chemicals from CO₂ could have a small but significant positive impact on the global carbon balance.

Up to recently, methane conversion has been developed into C₂ hydrocarbons via oxidative coupling of methane with oxygen as an oxidant, known as O₂ OCM hereafter, (Krylov and Mamedov, 1995; Al-Zahrani, 2001; Wolf, 1992) or carbon dioxide as an oxidant, known as CO₂ OCM hereafter, (Asami et al., 1995, 1997; Wang and Ohtsuka, 2000; Jiang et al., 2002), single step conversion to liquid fuels with oxygen (Eliasson et al., 2000; Huang et al., 2001b) or partially oxidized to methanol or formaldehyde (Lu et al., 1996). Another challenge of the natural gas processing is to convert it into more valuable products indirectly via synthesis gas formation via partial oxidation, steam reforming or CO₂ reforming of methane (Davis, 2001; Kulawska and Skrypek, 2001; Raje et al., 1997; Gesser and Hunter, 1998; Froment, 2000; Wilhelm et al., 2001). The various direct and indirect routes for the production of useful chemicals from natural gas are depicted in Figure 1.1 (Ross et al., 1996).

Figure 1.1  Various direct and indirect routes for the production of useful chemicals from natural gas
The C₂ hydrocarbons involve acetylene, ethylene and ethane, where ethane is primary used for the formation of ethylene by dehydrogenation, and ethylene has largely replaced acetylene as a petrochemical source. The United States alone produces nearly 60 billion pounds of ethylene per year (Gordon et al., 2001). Ethylene is highly reactive, due to its double bond, allowing it to be converted to a large variety of products by addition, oxidative and polymerization reactions, such as high and low density polyethylene, ethylene dichloride, ethylene glycol, ethylene oxide, ethylbenzene, vinyl acetate, polyvinyl chloride and polyesters (Kniel et al., 1980) and to be oligomerized to liquid hydrocarbons.

Ethylene can be derived from many different feedstocks. Ethylene was originally manufactured by partial hydrogenation of acetylene, dehydration of ethanol, or low temperature decomposition of coke-oven gas (Weissermel and Arpe, 2003). The feedstock and the resulting process vary which is dependent on the region. Figure 1.2 reveals different feedstocks used in the production of ethylene and their relative amounts in United States (Gordon et al., 2001). However, for Western Europe and Japan naphta is the primary feedstock for the production of ethylene since natural gas is less abundant (Weissermel and Arpe, 2003).

**Figure 1.2** Ethylene feedstocks in the United States (in billion pounds) (Gordon et al., 2001)
Recently, the thermal cracking of petroleum-based naptha with steam, known as pyrolysis, was used for over 97% of the worldwide production of ethylene. This process uses a feed stream that is a mixture of hydrocarbons and steam. The feed stream is preheated to a temperature of 773-923 K and then raised to 1023-1148 K in controlled manner in a radiant tube (Centi et al., 2001). In the radiant tube, the hydrocarbons crack into the major products (ethylene, olefins, and diolefins). Due to the high temperatures required for the endothermic reaction, an intensive energy input is required to drive the process. The production of ethylene from ethane was also done by steam cracking. A typical ethane process operates near 60% conversion of ethane and achieves an ethylene selectivity of 85% (Gordon et al., 2001). Over 10% of the ethane is thereby converted into carbon dioxide, and nitrogen oxides are also formed by the combustion. Production of ethylene by steam cracking is a large contributor to the greenhouse gases. It is a challenge to introduce the technologies that will reduce the emission of greenhouse gases during the production of ethylene.

1.1.1 Carbon Dioxide Reforming of Methane

Carbon dioxide reforming converts methane to synthesis gas with low $H_2/CO$ ratio ($H_2/CO \approx 1$). Therefore, the synthesis gas is used for production of liquid hydrocarbon in Fischer-Tropsch synthesis network. Carbon dioxide reforming of methane (CORM) is also known as dry reforming of methane due to the use of $CO_2$ gas instead of steam. The reaction scheme of CORM is depicted in Equation (1.1).

$$ CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H^0_{298} = +247 \text{ kJ/mol} \quad (1.1) $$

However, simultaneously the $H_2$ product can react with $CO_2$ to form CO and $H_2O$, namely Reverse Water Gas Shift (RWGS) reaction, as depicted in Equation (1.2). The RWGS reaction reduces the $H_2$ product and causes decrement of $H_2/CO$ ratio.

$$ CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H^0_{298} = +41 \text{ kJ/mol} \quad (1.2) $$
Among the direct routes, the CORM produces the lowest hydrogen content in
the synthesis gas (Ross et al., 1996). The CORM is a very reasonable route for the
chemical production according to the low H₂/CO ratio that is very effective for
further synthesis of valuable oxychemical as reported by Stagg-Williams (1999) and
suitable for Fischer-Tropsch process.

1.1.2 Carbon Dioxide Oxidative Coupling of Methane

The oxidative coupling of methane (OCM) is a promising and a novel route
for the conversion of methane to C₂ hydrocarbons in the presence of basic catalyst at
temperature 923 to 1123 K (Choudhary et al., 1999). Several studies have been
reported owing to the catalytic OCM using O₂ (O₂ OCM) as an oxidant (Wolf et al.,
1992; Davydov et al., 1995; Barchert and Baerns, 1997; Johnson et al., 1997; Zeng et
al., 2001; Krylov and Mamedov, 1995; Lunsford, 2000) since its high reactivity
toward oxidation reaction.

In O₂ OCM, the inevitable formation of CO and CO₂, however, seems to be
one of the most serious problems from practical point of view. Recently, carbon
dioxide has been used instead of oxygen as an oxidant in CO₂ OCM to produces
active oxygen species, which in turn activates methane to CH₃* radical (Amariglio et
al., 1998; Nozaki et al., 1990; Asami et al., 1995,1997; Krylov and Mamedov, 1995;
Pareja et al., 1998; Wang and Ohtsuka, 2001). Unlike oxygen, CO₂ does not induce
gas phase radical reactions (Wang and Ohtsuka, 2001). In other words, the reactions
of CH₄ and CO₂ to produce C₂ hydrocarbons are controlled by heterogeneous
catalysis. It is thus expected to develop an active catalyst having high selectivity to
C₂ hydrocarbons. Equations (1.3) and (1.4) are the two main reaction schemes for
CO₂ OCM to produce C₂ hydrocarbons with carbon monoxide and water as the by-
products.

\[
\begin{align*}
2\text{CH}_4 + \text{CO}_2 & \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O} \quad \Delta H^{\circ}_{298} = +106 \text{ kJ/mol} \quad (1.3) \\
2\text{CH}_4 + 2\text{CO}_2 & \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O} \quad \Delta H^{\circ}_{298} = +284 \text{ kJ/mol} \quad (1.4)
\end{align*}
\]
Moreover, equilibrium conversion of CH\textsubscript{4} to C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} from thermodynamic calculations was studied by Wang et al. (1999). The equilibrium conversion increased as the raising temperature and CO\textsubscript{2}/CH\textsubscript{4} ratio. High CO\textsubscript{2}/CH\textsubscript{4} ratio favours the CH\textsubscript{4} conversion to C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} and their yield exceed 15% and 25%, respectively at 1073 K for CO\textsubscript{2}/CH\textsubscript{4} reactant ratio of 2. The key point for realization is to develop an efficient catalyst, which is capable not only for activating both CH\textsubscript{4} and CO\textsubscript{2} but also for producing C\textsubscript{2} hydrocarbons selectively.

1.2 Current Catalyst Technology in CO\textsubscript{2} OCM

Direct methane and carbon dioxide conversion into C\textsubscript{2} hydrocarbons provides a novel route for simultaneous activation and utilization of methane and carbon oxides. The direct conversion of methane to more valuable chemicals has been an attractive task in catalytic studies by utilizing carbon dioxide as an oxidant. Among several processes, oxidative coupling of methane to ethane and ethylene has been studied most intensively (Asami et al., 1995, 1997; Wang et al., 1998a, 1998b; Wang et al., 1999; Wang and Ohtsuka, 2000, 2001; Jiang et al., 2002; Cai et al., 2003). The previous studies on CO\textsubscript{2} OCM are summarized in Table 1.3 which is presented historically.

Enhancement of C\textsubscript{2} hydrocarbons formation by CO\textsubscript{2} was first observed in the oxidative coupling of methane over a PbO/MgO catalyst, but it could not be sustained in the absence of O\textsubscript{2} (Wang and Zhu, 2004). Asami et al. (1995, 1997) systematically investigated the catalytic activities of more than 30 metal oxides for the conversion of CH\textsubscript{4} by CO\textsubscript{2} in the absence of O\textsubscript{2}. They found that lanthanide oxides generally showed higher activities. Among them, praseodymium oxide or terbium oxide exhibited relatively good catalytic performance with a C\textsubscript{2} yield of 1.5% and a selectivity of 50% at 1123 K. Wang et al. (1998c) further investigated the conversion of CH\textsubscript{4} to C\textsubscript{2}H\textsubscript{6} over praseodymium oxide and reported that the praseodymium oxide could be effective in the presence of CO\textsubscript{2} at temperatures as low as 773 – 923 K to form C\textsubscript{2} hydrocarbons.
In addition to the mono oxide, binary oxide catalysts were also investigated by several research groups for CO\textsubscript{2} OCM as presented in Table 1.3. From Table 1.3, a binary oxide (La\textsubscript{2}O\textsubscript{3}-ZnO) was observed to have high C\textsubscript{2} hydrocarbons selectivity and good stability, giving a C\textsubscript{2} yield of 2.8\% (Chen \textit{et al}., 1996). Although this yield is better than that of any monoxide system reported previously, it is still quite low. Wang \textit{et al}. (1998a, 1998b, 1999) investigated ceria that had been modified with alkali metal and alkaline earth metal oxides for the reaction and reported that CaO-CeO\textsubscript{2} catalyst systems are potential. They suggested that the C\textsubscript{2} yield could reach 6.1\% at 1173 K over the CaO-CeO\textsubscript{2} catalyst. Characterization of the system indicated that the redox of Ce\textsuperscript{4+}/Ce\textsuperscript{3+} is responsible for the activation of CO\textsubscript{2}, i.e. the dissociation to CO and oxygen species, which accounts for CH\textsubscript{4} conversion, and the basic Ca\textsuperscript{2+} ion in the catalyst greatly enhances the selectivity to C\textsubscript{2} hydrocarbons (Wang \textit{et al}., 1999). In the meantime, they also reported that CaO-Cr\textsubscript{2}O\textsubscript{3} catalysts are effective for this reaction (Wang \textit{et al}., 1998b).

Another binary catalyst of CaO-ZnO was also tested by the same group for the reaction (Wang and Ohtsuka, 2001). A C\textsubscript{2} selectivity being 80\% and a C\textsubscript{2} yield being 4.3\% were achieved over this catalyst with a Ca/Zn ratio of 0.5 at 1148 K. They suggested that the lattice oxygen of the CaO-ZnO catalyst could convert CH\textsubscript{4} mainly to H\textsubscript{2} and CO. The presence of CO\textsubscript{2} contributes to a new oxygen species, which is active and selective for the conversion of CH\textsubscript{4} to C\textsubscript{2} hydrocarbons. The CaO component in the catalyst enhances the adsorption of CO\textsubscript{2} and thus suppresses the reaction involving the lattice oxygen. The reduced-Zn site was suggested to activate CO\textsubscript{2} (Wang and Ohtsuka, 2000).
Table 1.3: Catalyst development for methane oxidative coupling with carbon dioxide to C₂ hydrocarbons

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temperature (K)</th>
<th>CH₄ Conversion (%)</th>
<th>CO₂/CH₄ Ratio</th>
<th>C₂ Hydrocarbons Selectivity (%)</th>
<th>C₂ Hydrocarbons Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂O₃-ZnO</td>
<td>1123</td>
<td>3.1</td>
<td>1.0</td>
<td>91</td>
<td>2.8</td>
<td>Chen et al., 1996</td>
</tr>
<tr>
<td>CaO-Cr₂O₃</td>
<td>1123</td>
<td>6.3</td>
<td>2.3</td>
<td>63</td>
<td>4.0</td>
<td>Wang et al., 1998b</td>
</tr>
<tr>
<td>CaO-MnO₂</td>
<td>1123</td>
<td>3.9</td>
<td>2.3</td>
<td>68</td>
<td>2.7</td>
<td>Wang et al., 1998b</td>
</tr>
<tr>
<td>Na₃WO₄-Mn/SiO₂</td>
<td>1093</td>
<td>4.7</td>
<td>2.0</td>
<td>94</td>
<td>4.5</td>
<td>Liu et al., 1998</td>
</tr>
<tr>
<td>CaO-CeO₂</td>
<td>1123</td>
<td>5.0</td>
<td>1.0</td>
<td>62</td>
<td>3.2</td>
<td>Wang et al., 1999</td>
</tr>
<tr>
<td>CaO-ZnO</td>
<td>1148</td>
<td>5.4</td>
<td>2.3</td>
<td>80</td>
<td>4.3</td>
<td>Wang and Ohtsuka, 2000</td>
</tr>
<tr>
<td>SrO-Cr₂O₃</td>
<td>1123</td>
<td>2.4</td>
<td>2.3</td>
<td>37</td>
<td>1.3</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>SrO-ZnO</td>
<td>1123</td>
<td>2.8</td>
<td>2.3</td>
<td>79</td>
<td>2.2</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>SrO-CeO₂</td>
<td>1123</td>
<td>1.5</td>
<td>2.3</td>
<td>64</td>
<td>1.0</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>SrO-MnO₂</td>
<td>1123</td>
<td>3.9</td>
<td>2.3</td>
<td>85</td>
<td>3.3</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>BaO-ZnO</td>
<td>1123</td>
<td>0.6</td>
<td>2.3</td>
<td>74</td>
<td>0.4</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>BaO-CeO₂</td>
<td>1123</td>
<td>0.4</td>
<td>2.3</td>
<td>55</td>
<td>0.2</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>BaO-Cr₂O₃</td>
<td>1123</td>
<td>0.8</td>
<td>2.3</td>
<td>42</td>
<td>0.3</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>BaO-MnO₂</td>
<td>1123</td>
<td>3.8</td>
<td>2.3</td>
<td>67</td>
<td>2.6</td>
<td>Wang and Ohtsuka, 2001</td>
</tr>
<tr>
<td>MnO₂-SrCO₃</td>
<td>1148</td>
<td>5.7</td>
<td>2.3</td>
<td>51</td>
<td>4.5</td>
<td>Cai et al., 2003</td>
</tr>
<tr>
<td>Nano-sized CeO₂-ZnO</td>
<td>1098</td>
<td>5.7</td>
<td>2.0</td>
<td>83.6</td>
<td>4.8</td>
<td>He et al., 2004</td>
</tr>
</tbody>
</table>
Moreover, Wang and Ohtsuka (2001) further reported their investigations of catalytic performance and kinetics over other binary oxides, mainly CaO-MnO$_2$ (Wang et al., 1998b), SrO-MnO$_2$, and BaO-MnO$_2$, for the CO$_2$ OCM process. At temperatures above 1113 K, the CaO-MnO$_2$ catalyst exhibited a performance similar to that of other calcium-containing binary oxide catalysts (CaO-CeO$_2$, CaO-Cr$_2$O$_3$, and CaO-ZnO). It was reported that C$_2$ selectivity and yield at 1123 K increased remarkably with increasing partial pressure of CO$_2$, and apparent activation energies observed over these catalysts were approximately similar (190-220 kJ/mole) (Wang and Ohtsuka, 2001; Wang et al., 1998b). When the temperature decreased from 1113 to 1098 K, CH$_4$ conversion and C$_2$ selectivity over the CaO-MnO$_2$ catalyst abruptly decreased and a discontinuous change was also observed in the Arrhenius plots. On the other hand, the SrO-MnO$_2$ and BaO-MnO$_2$ catalysts exhibited kinetic features different from the CaO-MnO$_2$ system, in which the C$_2$ selectivity at 1123 K changed only slightly with the partial pressure of CO$_2$. It was also revealed that the activation energies were constant over the entire temperature range examined and notably lowered. From characterization results, a solid solution of Ca$_{0.48}$Mn$_{0.52}$O was the main phase for the CaO-MnO$_2$ catalyst after reaction at 1123 K, whereas, at 1073 K, some Ca$^{2+}$ ions were separated from the solid solution to form CaCO$_3$, which covered the catalyst surface. With the SrO-MnO$_2$ and BaO-MnO$_2$ catalysts, SrCO$_3$ and BaCO$_3$ were formed, along with MnO$_2$ after reaction and the carbonates were suggested to react with MnO$_2$ to form SrMnO$_{2.5}$ and BaMnO$_{2.5}$ in the conversion process of CH$_4$ with CO$_2$ (Wang and Ohtsuka, 2001). Cai et al. (2003) further investigated the system of Mn/SrCO$_3$ with a Mn/Sr ratio of 0.1 and 0.2 for the selective conversion of CH$_4$ to C$_2$ hydrocarbons using CO$_2$ as an oxidant and achieved C$_2$ selectivities of 88% and 79.1% at 1148 K with a C$_2$ yield of 4.3% and 4.5%, respectively. Recently, He et al. (2004) investigated a nano-CeO$_2$/ZnO catalyst using a novel combination of homogeneous precipitation with micro-emulsion. Their experimental results demonstrated that methane conversion over the nano-CeO$_2$/ZnO catalyst was higher than that obtained over catalysts prepared by conventional impregnation. They reported that when the content of ZnO was 33%, the methane conversion was 5.73% with C$_2$ hydrocarbons selectivity of 83.6% at reaction temperature 1098 K. The yield of C$_2$ hydrocarbons achieved 4.79%. Unfortunately, more coke was formed on the surface of catalysts at higher temperatures. Pertaining to ternary metal oxide catalyst, Na$_2$WO$_4$-Mn/SiO$_2$ catalyst
was further investigated in the conversion of CH$_4$ with CO$_2$ to C$_2$ hydrocarbons (Liu et al., 1998). A C$_2$ yield and selectivity of about 4.5% and 94%, respectively were obtained at 1093 K (Liu et al., 1998).

Zhang et al. (2002a) recently reported using pulse corona plasma as an activation method and applied it for the reaction of CH$_4$ and CO$_2$ over some catalysts. The products were C$_2$ hydrocarbons and the by-products were CO and H$_2$. CH$_4$ conversion and C$_2$ hydrocarbons yield were affected by the CO$_2$ concentration in the feed. The CH$_4$ conversion increased as the CO$_2$ concentration in the feed increased, while C$_2$ hydrocarbons yield decreased. The synergism of La$_2$O$_3$/$\gamma$-Al$_2$O$_3$ and plasma gave a CH$_4$ conversion of 24.9% and C$_2$ hydrocarbons yield of 18.1% were obtained at a plasma power input of 30 W. The distribution of C$_2$ hydrocarbons was changed through the use of a Pd-La$_2$O$_3$/$\gamma$-Al$_2$O$_3$ catalyst and the major C$_2$ product was ethylene. It is noted that the synergetic effect of catalyst and plasma improves the performance of CH$_4$ and CO$_2$ conversion to C$_2$ hydrocarbons.

1.3 Basic Principles of Heterogeneous Catalysis

1.3.1 Concept of Catalysis

A catalyst is a substance that affects the rate of a reaction but not consumed. The catalyst usually changes a reaction rate by promoting a different molecular path (mechanism) for the reaction which gives lower its activation energy. The reaction coordinate to measure the progress along the reaction and pass over the activation energy barrier is depicted schematically in Figure 1.3. The development and use of catalysts is a major part of the constant search for new ways of enhancing product yield and selectivity of chemical reactions. The catalyst can affect both yield and selectivity, because it is possible to obtain an end product by a different pathway (with lower energy barrier). Indeed, a catalyst changes only the rate of a reaction, but it does not affect the equilibrium.
Homogeneous catalysis concerns processes in which a catalyst is in solution with at least one of the reactants. A heterogeneous catalytic process involves more than one phase. Usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. The simple and complete separation of the fluid product mixture from the solid catalyst makes heterogeneous catalysis economically attractive. A heterogeneous catalytic reaction occurs at or very near the fluid-solid interface. The principles that govern heterogeneous catalytic reactions can be applied to both catalytic and noncatalytic fluid-solid reactions. There are two other types of heterogeneous reactions involve gas-liquid and gas-liquid-solid system. Reaction between gas and liquid systems are usually mass-transfer limited.

Since a catalytic reaction occurs at fluid-solid interface, a large interfacial area can be helpful or even essential in attaining a significant reaction rate. In many catalysts, this area is provided by a porous structure, where the solid contains many fine pores, and the surface supplies the area needed for the high rate of reaction. The area possessed by some porous materials is surprisingly large. The catalyst that has a large area resulting from pores is called a porous catalyst. Sometimes pores are so small that they will admit small molecules but prevent large ones from entering. Materials with this type of pore are called molecular sieves, and they may be derived.

**Figure 1.3** Energy activation of a reaction along the reaction coordinate (Fogler, 1999).
from natural substances such as certain clays and zeolites, or be totally synthetic, such as some crystalline aluminosilicates.

In some cases a catalyst consists of minute particles of an active material dispersed over a less active substance called a support. The active material is frequently a pure metal or metal alloy. Such catalysts are called supported catalysts, as distinguished from unsupported catalysts, whose active ingredients are major amounts of other substances called promoters, which increase the activity.

Pertaining to gas-phase reactions catalyzed by solid surfaces, at least one and frequently all of the reactants must become attached to the surface. This attachment is known as adsorption and takes place by two different processes: physical adsorption and chemisorption. Physical adsorption is similar to condensation, where the process is exothermic and the heat of adsorption is relatively small. The force of attraction between the gas molecules and the solid surface are weak. These van der Waals forces consist of interaction between permanent dipoles, between a permanent dipole and an induced dipole, and/or between neutral atoms and molecules (Centi et al., 2001). The amount of gas physically adsorbed decreases rapidly with increasing temperature, and above its critical temperature only very small amounts of a substance are physically adsorbed. The type of adsorption that affects the rate of a chemical reaction is chemisorption. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occurs between bonded atoms in molecules. As a result the electronic structure of the chemisorbed molecule is perturbed significantly, causing it to be extremely reactive. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are generally of the same magnitude as the heat of a chemical reaction. If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

A reaction is not catalyzed over the entire solid surface but only at certain active sites or centres. The active sites can also be thought of as places where highly reactive intermediates (chemisorbed species) are stabilized long enough to react. It is defined that an active site as a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule (Centi et al., 2001). One
parameter used to quantify the activity of a catalyst is the turnover frequency. The
turnover frequency is the number of molecules reacting per active site per second at
the conditions of the experiment. The dispersion of the catalyst is the fraction of the
metal atoms deposited that are on the surface. The interaction of reactants with the
catalyst surface is a key parameter in heterogeneous reaction systems. For example,
the temperature at which species are desorbed from a surface is indicative of the
strength of the surface bond where the higher the temperature, the stronger the bond.
Therefore the adsorption of a probe molecule at low temperature, and subsequent
monitoring of its desorption/reaction characteristics with temperature, is a simply
way to characterize surface properties of catalysts and adsorbents.

1.3.2 Point Defects in the Catalyst Structure

Gellings and Bouwmeester (2000) reported an overview study of the defects
on catalyst structure. The defects under consideration here may be vacant lattice
sites (vacancies), ions placed at normally unoccupied sites (interstitial ions), foreign
ions present as impurity or dopant and ions with charges different from those
expected from the overall stoichiometry. Electron defects may arise either in the
form of ions present with charges deviating from the normal lattice ions, or as a
consequence of the transition of electrons from normally filled energy levels, usually
the valence band, to normally empty levels, the conduction band. In those cases
where an electron is missing, i.e. when there is an electron deficiency, this is usually
called an electron hole or hole (h⁺). Usually it is convenient to consider point
defects, such as vacancies or electron hole, to be the moving entities in a lattice even
though in reality of course the ions or electrons move through the lattice in the
opposite direction. The charges of defects and of the regular lattice particles are
defined with respect to the neutral, unperturbed (ideal) lattice and are called effective
charges. These are indicated by a dot (’) for a positive excess charge, by a prime (‘)
for a negative excess charge and by an x (x) for effectively neutral defects (Gellings
and Bouwmeester, 2000).
Moreover, Gellings and Bouwmeester (2000) reported on oxidative coupling of methane over CaO-CeO$_2$ catalysts. With increasing doping of CeO$_2$ with CaO the concentration of oxygen vacancies and thus of the oxygen ion conductivity increases strongly through the substitution reaction where Ca$^{2+}$ ions are placed on Ce$^{4+}$ sites under formation of Ca$_{x}$ ions, with charge compensation by oxygen vacancies. Kaspar et al. (1999) and Terribile et al. (1999) suggested that the introduction of relatively small amount of smaller Zr$^{4+}$ or Mn$^{3+}/^{4+}$ into CeO$_2$ generates defects throughout the matter and brings about an increase of oxygen mobility and pronounces the increasing reducibility of CeO$_2$.

### 1.3.3 Role of Acid-Base Properties in Catalytic Oxidation

In addition to the redox properties, transition metal oxides are characterized by the presence of acid-base properties (Centi et al., 2001) which also can play a significant role in oxidation reactions. It is thus quite reasonable that in the past many attempts have been made to find correlations between acid-base properties and redox characteristics and catalytic reactivity. The ideal surface structure of an oxide is composed by an array of cations and oxygens, some of which are coordinatively unsaturated and accessible to gas reactants, and thus generate Lewis and Brønsted acidic or basic sites. The strength and number of these sites depend on the nature of the cation, the type of metal to oxygen bond, and the packing of the specific crystalline plane.

The study of the acid-base characteristics and their possible influence on catalytic behaviour is crucial for a better understanding of the surface processes and their control to improve selectivity and reactivity. The acid-base properties of catalyst have three primary roles in relation to the catalytic behaviour (Centi et al., 2001): (i) influence on the activation of the hydrocarbons molecule, (ii) influence on the rates of competitive pathways of transformation, and (iii) influence on the rate of adsorption and desorption of reactants and products. Two further ideas may be cited on the topic of the surface reaction mechanisms of selective oxidation:
(1). The combination of acid-base and redox properties of the oxide surface determines the mechanism of transformation

(2). The nature of the oxygen species on the catalyst determines the kind of selectivity.

In the process of oxygen incorporation into the oxide structure, various type of electrophilic activated oxygen species form before being incorporated as structural (lattice) oxygen of the oxide. The latter has a nucleophilic character and gives rise to a different type of attack on an adsorbed alkene and thus different types of products.

In the process of incorporation of catalyst structural oxygen into the organic molecule, a point defect forms, which can be compensated for by a change in the linkage of the coordination polyhedra. If the latter process is not a rapid one, and the replenishment of surface oxygen vacancies through oxygen bulk diffusion is also slow, the population of surface electrophilic oxygen species increases with lowering of the selectivity to partial oxidation products. The selectivity is thus a function of the surface geometry of active sites and the redox properties of the catalyst.

1.3.4 Surface Oxygen Species and Their Role in Selective Oxidation

The nature of the surface oxygen species and their reactivity and role in catalysis is obviously a crucial theme in selective oxidation. There are two basic types of oxygen species:

1. Lattice oxygen, which can be either terminal (M=O) or bridging (M-O-M1) oxygen. Further difference arises not only from the strength of these metal-oxygen bonds, which depends on the nature and valence state of the transition metal but also from the coordination of the metal-oxygen polyhedra.

2. Adsorbed radical-type oxygen, formed in the process of the reduction of gaseous O$_2$ to lattice O$^{2-}$ due to electron transfer from the metal to the oxygen. These species are stabilized by coordination with surface metal ions. During this transformation the nature of the metal-oxygen bond and its polarizability change from an electrophilic character for the negatively charged species to a nucleophilic character for structural O$^{2-}$. 
In general, the reactivity of adsorbed oxygen species has been studied for simple once-through reactions, in which the oxygen species are consumed but no renewed. Oxygen can be involved in oxidation reactions in at least three distinct ways, more than one of which may be operative in any reaction mechanism. The first is the abstraction of a hydrogen from an adsorbed organic molecule to give a radical or carbanion on the surface. The second is the attack on the organic species by a negatively charged oxygen ion whether lattice oxygen or adsorbed oxygen, and the third is the replenishment of lattice oxygen that has been used in a direct oxidation reaction. There are a number of oxygen species: $\text{O}_2$ (adsorbed molecule), $\text{O}$ (adsorbed neutral atom), $\text{O}_2^\cdot$ (superoxide), $\text{O}_2^{2\cdot}$ (peroxide), $\text{O}_3^\cdot$ (ozonide), $\text{O}^\cdot$, etc. which may be present on the catalyst surface (Gellings and Bouwmeester, 2000).

A highly basic catalyst is believed to enhance carbon dioxide adsorption, which is then activated on oxygen vacancies to form oxygen active species and gaseous carbon monoxide according to Equations (1.5) and (1.6) using the Kröger-Vink notation (Gellings and Bouwmeester, 2000).

\[
\begin{align*}
\text{V}_o^{\bullet\bullet} + 2\text{CO}_2 \text{(gas)} & \rightleftharpoons 2 \text{O}_o^\cdot + 2\text{CO} \text{(gas)} \quad (1.5) \\
\text{V}_o^{\bullet\bullet} + 2\text{CO}_2 \text{(gas)} & \rightleftharpoons 2 \text{O}_o^\bullet + 2\text{CO} \text{(gas)} + 2\text{h}^\cdot \quad (1.6)
\end{align*}
\]

In the Equations (1.5) and (1.6), $\text{V}_o^{\bullet\bullet}$ denotes vacancies which will be occupied by doubly ionized oxygen, $\text{h}^\cdot$ denotes electron holes, $\text{O}_o^\bullet$ denotes oxygen ion on neutral lattice positions and $\text{O}_o^\cdot$ denotes single ionized oxygen on oxygen vacancies as active oxygen species.

### 1.3.5 Cerium oxide as a Catalyst for CO$_2$ OCM

Recently, cerium oxide or ceria ($\text{CeO}_2$) plays significant roles in several catalytic processes. Under various redox conditions, the oxidation state of ceria may vary between +3 and +4. Owing to its nonstoichiometric behaviour, $\text{CeO}_2$ has
proved to be a good promoter for oxygen storage in addition to the stabilization of the metals dispersion (Fornasiero et al., 1995). Kaspar et al. (1999) suggested that different cations having ionic radii smaller than Ce\(^{4+}\) effectively stabilized the CeO\(_2\) against sintering, while all dopants whose radii are larger than Ce\(^{4+}\) significantly stabilize with respect to high temperature calcination which means that thermal stabilization of CeO\(_2\) is enhanced. Insertion of a low-valent ion should enhance the oxygen anion mobility in the CeO\(_2\) and increasing the oxygen storage capacity of these materials (Kaspar et al., 1999). Two type of oxygen vacancies are created in the doped ceria: intrinsic and extrinsic. The former is due to the reduction of Ce\(^{4+}\) according to the following reaction:

\[
2\text{Ce}^{x+}_{\text{Ce}} + O_0 \rightarrow 2\text{Ce}^{1+}_{\text{Ce}} + \text{V}^{x+}_O + \frac{1}{2}O_2
\]  

(1.7)

while the latter is created by the insertion of the bi- or tri-valent cation according to the following reactions (M denotes metal):

\[
\text{MO} \rightarrow M^{2+}_{\text{Ce}} + \text{V}^{x+}_O + \frac{1}{2}O_2
\]  

(1.8)

\[
\text{M}_2\text{O}_3 \rightarrow 2M^{2+}_{\text{Ce}} + 2O^x_0 + \text{V}^{x+}_O + \frac{1}{2}O_2
\]  

(1.9)

Most researchers concluded that the oxidation/reduction reaction of Ce\(^{4+}/\text{Ce}^{3+}\) is effective to activate carbon dioxide to form oxygen active species which in turn it activate methane (Wang and Ohtsuka, 2001; Wang et al., 1998a, 1998b; Cai et al., 2003). The C\(_2\) hydrocarbons selectivity may be contributed by the catalyst basicity or the basic sites distribution. This may be due to enhancement of CO\(_2\) chemisorptions on the basic sites in the catalyst surface. CeO\(_2\) have excellent redox properties owing to the very fast reduction of Ce\(^{4+}/\text{Ce}^{3+}\), which is associated to the formation of oxygen vacancies at the surface. The oxygen mobility and reducibility of CeO\(_2\)-based catalyst can be enhanced by loading transition metal oxide (MnO or WO\(_3\)). The addition of transition metal oxides may increase the oxygen vacancy centres, which may be responsible for CO\(_2\) activation to oxygen active species. This phenomenon is inline with suggestion from Kaspar et al. (1999) and Terribile et al. (1999) where the introduction of relatively small amount of smaller Zr\(^{4+}\) or Mn\(^{3+}/4+\) into CeO\(_2\) generates defects and brings about an increase of oxygen mobility and pronounces the increasing reducibility of CeO\(_2\). Leitunburg et al. (1997) concluded that reduced ceria has a strong effect on CO\(_2\) adsorption and activation. They
suggested that oxygen vacancies, and particularly those present in the bulk, are the driving force for CO$_2$ activation with the formation of CO and oxidation of reduced ceria.

1.4 Problem of Research

Oxidative coupling of methane is one of the attractive routes for the conversion of methane to higher hydrocarbons via radical formation. The reaction can be carried out by either reducible or non-reducible metal oxide with a feed of methane where lattice oxygen is used as an oxidant or with a co-feed of oxygen or carbon dioxide. However, oxygen unavoidably induces some gas phase radical reaction which causes low C$_2$ hydrocarbons yield due to reducing methyl radical. However, almost previous research on the CO$_2$ OCM still exhibited quite low methane conversion and C$_2$ hydrocarbons yield (Asami et al., 1995, 1997; Wang et al., 1998a, 1998b, 1999; Wang and Ohtsuka, 2000, 2001; Cai et al., 2003; He et al., 2004). The highest CH$_4$ conversion of 5.7% at 1123 K suggested that the conventional catalyst systems are not effective in activating CH$_4$ in CO$_2$ OCM. Therefore it is a great challenge to develop a new catalyst system or to find a new reaction method for the activation of CH$_4$ and CO$_2$ to produce C$_2$ hydrocarbons. The new catalyst and/or suitable reactor system can enhance the activation of CO$_2$ and CH$_4$ in order to improve the catalytic performances.

It is believed that carbon dioxide chemisorption is favoured on alkaline earth metal oxides (CaO) rather than other metal oxides (Tanabe et al., 1989). However, a strong basic oxide (i.e. SrO, BaO) will not favour the activation of CH$_4$ (Choudhary et al., 1999) due to the quite amount of carbon dioxide adsorbed which thus blocked the active sites of catalyst. An active oxygen species (O$^+$) produced from CO$_2$ activation are important in CO$_2$ OCM in activation of methane. A synergistic effect of oxidation/reduction mechanism and basicity of the catalyst may have a relationship with the CO$_2$ activation. The reducibility of CeO$_2$ catalyst could be enhanced by introduction of manganese oxide (MnO$_x$), while the catalyst basicity could be controlled by doping CaO. Higher reducibility of catalyst leads to
contribution of oxygen vacancies, which are active sites for CO₂ chemisorption. The plentiful of CO₂-adsorbed on the catalyst surface favours the reaction suppression involving the lattice oxygen and enhances the selective conversion of methane to C₂+-hydrocarbons. However, when only a few CO₂ is chemisorbed, some lattice oxygen would partially take part in the reaction and convert CH₄ mainly to H₂ and CO leading to low C₂ selectivity.

The optimal catalyst compositions in the CeO₂-supported catalyst and the optimal operating parameters, such as the CO₂/CH₄ ratio and reactor temperature, provide essential information for kinetic studies and for implementing the CO₂ OCM process to an industrial scale. From the fact that only low methane conversion and C₂ yield were addressed in the conventional fixed bed reactor, the modification of the reactor such that the methane and carbon dioxide activation in the catalyst surface could be enhanced is required.

1.5 Objectives of Research

The objectives of research are:
a) To study the feasibility of CO₂ OCM reaction via thermodynamic equilibrium analysis
b) To develop a suitable catalyst for CO₂ OCM process with high methane conversion and high selectivity toward C₂ hydrocarbons formation.
c) To investigate the synergistic effect of basicity and reducibility of the catalyst on catalytic activity of CO₂ OCM.
d) To optimize the catalyst compositions and operating conditions including their interaction effect suitable for the CO₂ OCM process.
e) To develop a high performance reactor system suitable for CO₂ OCM process.
1.6 Scopes of Research

The scopes of research are:

a) Thermodynamic equilibrium analysis is conducted to study the feasibility of all possible CH$_4$ and CO$_2$ reactions particularly for CO$_2$ OCM reaction.
b) Catalyst screening is performed on CeO$_2$-based catalysts for addressing the promising catalyst of CO$_2$ OCM process.
c) Catalyst characterizations are conducted on the fresh and/or used catalysts using XRD, FT-IR, Raman, CO$_2$-TPD, H$_2$-TPR in order to investigate the surface structure, basicity and reducibility of the catalysts.
d) Testing of the catalyst for CO$_2$ OCM reaction is carried out in a fixed-bed quartz reactor with the certain ranges of operating conditions at fixed atmospheric pressure.
e) The single- and multi-response optimizations are conducted to obtain the optimal catalyst compositions and operating conditions, which gives highly performance toward CO$_2$ OCM process.
f) The modification of reactor system is intended to achieve high catalytic performance of CO$_2$ OCM using a hybrid catalytic-dielectric barrier discharge (DBD) plasma reactor. The plasma reactor is aimed to enhance the methane and carbon dioxide activation at lower gas temperatures.

1.7 Organization of Thesis

The research is targeted on the development of a suitable catalyst and a high performance reactor system for CO$_2$ OCM process. The optimization of catalyst compositions and operating conditions and their interaction effect are discussed. The reactor modification is designed to improve the methane and carbon dioxide conversions using a hybrid catalytic-plasma reactor concept.

This thesis consists of eight chapters. Chapter 1 presents the background, literature review related to CO$_2$ OCM and basic principles of catalysis, research problem, objectives and scopes of the thesis. In Chapter 2, the general description of
research methodology and the detail experimental strategy are described. Thermodynamic studies on co-generation of C\textsubscript{2} hydrocarbon and synthesis gas from methane and carbon dioxide using direct minimization Gibbs free energy are presented in Chapter 3. Meanwhile, Chapter 4 introduces catalyst screening of CeO\textsubscript{2}-based catalysts to provide suitable catalyst for CO\textsubscript{2} OCM, at which some catalyst characterization methods such as FT-IR and Raman spectroscopies were implemented to confirm the surface structure of metal oxides. In this chapter, the CeO\textsubscript{2}-based catalyst was addressed as a promising catalyst for the CO\textsubscript{2} OCM. Some catalyst characterization method, i.e. X-ray Diffraction (XRD), H\textsubscript{2}-TPR and CO\textsubscript{2}-TPD, were applied to investigate the synergistic effect of catalyst basicity and reducibility toward CO\textsubscript{2} OCM process as presented in Chapter 5. In Chapter 6, the optimization of catalyst compositions and operating conditions for the selected catalyst are clearly explored owing to single- and multi-responses optimizations. Here, a new hybrid numerical algorithm is developed for solving the multi-responses optimization. The reactor modification using a hybrid catalytic-Dielectric Barrier Discharge (DBD) plasma reactor at low temperature is addressed in Chapter 7. Finally, Chapter 8 presents the main conclusions of this thesis and recommendations for future work.


