DUAL BED CATALYTIC REACTOR SYSTEM FOR DIRECT CONVERSION OF METHANE TO LIQUID HYDROCARBONS

SRIRAJ A/L AMMASI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

DECEMBER 2005

ABSTRACT

The feasibility of upgrading natural gas that primarily consists of methane to valuable chemicals, especially liquid fuel has been investigated for years. However, the high cost and inefficient processes have hampered the widespread exploitation of natural gas. Accordingly, a system comprising of a dual-bed catalytic has been investigated in this study to overcome the limitations and permit the direct conversion of methane to liquid hydrocarbons. In this dual-bed system, methane is converted in the first stage to Oxidative Coupling of Methane(OCM) products over La/MgO and the second bed comprises of H-ZSM-5 that has been tested as an oligomerization function to convert the OCM products to liquid hydrocarbons. The influence of SiO_2/Al_2O_3 ratio of H-ZSM-5, temperature and CH_4/O_2 ratio on the process has been studied. The results implied that the Bronsted acid sites of H-ZSM-5 were the active centers responsible for the oligomerization of primary ethylene products. Oxygen was absolutely necessary for the formation of the methyl radicals from methane, but it should be provided at a controllable manner in order to avoid undesired oxidation. The partial destruction and dealumination of H-ZSM-5 at higher temperature had caused the deactivation of the H-ZSM-5 catalyst for the oligomerization reaction. Investigation on the catalytic activity of various metals loaded H-ZSM-5 showed that incorporating nickel into H-ZSM-5 significantly enhances the yield of liquid hydrocarbons. The central composite design (CCD) coupled with response surface methodology (RSM) was successfully applied to map the response and to obtain the optimal reaction design. The results indicated that the optimum C_{5+} yield of 8.91% was attained at reaction temperature = 742 ºC, CH_4/O_2 ratio = 9.7 and Ni loading = 0.67 wt%. This exploration suggests that the concept of this dual-bed catalytic system is an interesting candidate for application in methane utilization to produce liquid hydrocarbons.

ABSTRAK

Keupayaan untuk mempertingkatkan gas asli yang mempunyai metana sebagai komponen utama kepada bahan kimia yang bernilai terutamanya cecair bahanapi telah diuji beberapa tahun yang lalu. Namun demikian, kos pengendalian yang tinggi dan ketidakcekapan proses telah menghadkan pengeksploitasian meluas gas asli. Sejajar dengan itu, sistem yang mengandungi dua lapisan mangkin telah dicadangkan dalam penyelidikan ini untuk mengatasi masalah tersebut dan membolehkan penukaran terus metana kepada cecair hidrokarbon. Dalam sistem dua lapisan mangkin ini, metana ditukarkan kepada produk pengoksidaan berpasangan metana (OCM) pada peringkat pertama dan seterusnya lapisan kedua yang mengandungi H-ZSM-5 telah diuji untuk berperanan dalam tindak balas pengoligomeran untuk menukarkan produk OCM kepada cecair hidrokarbon. Pengaruh nisbah SiO_2/Al_2O_3 pada H-ZSM-5, suhu dan nisbah CH_4/O_2 ke atas proses telah dikaji. Keputusan eksperimen membuktikan bahawa asid *Bronsted* pada H-ZSM-5 bertindak sebagai pusat yang aktif yang berfungsi kepada tindak balas oligomerasi etena. Oksigen sangat diperlukan untuk pembentukan radikal metil daripada metana tetapi ia perlu dibekalkan pada tahap yang sesuai untuk mengelakkan pengoksidaan yang tidak diingini. Suhu tindak balas yang tinggi akan mengakibatkan kemusnahan separa dan dealuminasi HZSM-5 yang mengurangkan keaktifan mangkin untuk tidak balas oligomerasi. Kajian ke atas aktiviti mangkin H-ZSM-5 yang mengandungi logam sebagai fungsi tambahan kepada fungsi asid menunjukkan bahawa penambahan nikel pada H-ZSM-5 jelas meningkatkan kepemilihan cecair hidrokarbon. Rekabentuk *Central composite design* (CCD) bergandingan dengan *response surface methodology* (RSM) telah digunakan dengan jayanya untuk melakarkan respon dan untuk mendapatkan rekabentuk optimum tindak balas. Keputusan menunjukkan bahawa nilai optimum kepemilihan C_{5+} ialah 8.91% yang dicapai pada suhu= 742 ^{0}C, nisbah CH_4/O_2=9.7 dan muatan nikel=0.67%berat. Kajian ini mencadangkan bahawa konsep yang mempunyai dua lapisan mangkin adalah satu rekabentuk yang menarik untuk digunakan dalam penukaran metana kepada cecair hidrokarbon.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

a_{iC} - The number of atoms of the carbon presents in each molecule of the chemical species i
Å - Angstrom
^0C - Degree Celsius
F - The ratio of mean squares due to regression to mean squares due to residual
F_i - Gas species i flowrate
k - Number of independent variables
K - Kelvin degree
n_o - The number of experiments repeated at the center point
p - The number of terms in the fitted model
R^2 - The determinant of coefficient
w - The number of water molecules per unit cell
x_1 - The coded forms of input variables for operating temperature
x_2 - The coded forms of input variables for CH_4/O_2 ratio
x_3 - The coded forms of input variables for amount of nickel loading
X_i, X_j - The independent variables
Y - Experimental values of yield C_{5+}
y - Mol fraction
¥ - The predicted yield of C_{5+}
α - Star point value
$\beta_1, \beta_2, \beta_3$ - The linear terms
$\beta_{11}, \beta_{22}, \beta_{33}$ - The squared terms
$\beta_{12}, \beta_{13}, \beta_{23}$ - The interaction terms
β_o - The offset term

LIST OF ABBREVIATIONS

AGC-21 - Advanced Gas Conversion for the 21st Century
ANOVA - Analysis of variance
BET - Brunauer-Emmett-Teller's surface area model
CCD - Central composite design
CNG - Compressed natural gas
DOE - Design of experiments
ESR - Epsilon Serializability Resonance
FCC - Fluid catalytic cracking
FID - Flame Ionization Detector
GC - Gas chromatography
GTL - Gas to Liquids technologies
HT - Hydrogen transfer
I.D. - Internal diameter
LNG - Liquefied natural gas
M - Metal
MFI - Mobil Five Topology
MTG - Methanol to gasoline
NA - Nitrogen adsorption
NGV - Natural gas vehicles
NMR - Nuclear Magnetic Resonance
NNN - Nearest neighbour positions
OCM - Oxidative Coupling of Methane
ODH - Oxidative Dehydrogenation
NODH - Non-Oxidative Dehydrogenation
PIONA Paraffins, Iso-paraffins, Olefins, Naphtha, and Aromatics
REM - Rare-earth-metal
RON - Research Octane Number

RSM	-	Response surface methodology
S.S	-	Sum of square
SBU	-	Smallest number of TO_4 units
SHOP	-	Shell higher olefin process
SMDS	-	Shell Middle Distillate Synthesis
SSE	-	Squares of the error
SSR	-	Squares due to regression
SST	-	Sum of squares
Syngas	-	Synthesis gas
TCD	-	Thermal conductivity detector
TPD	-	Temperature programmed desorption
TPR	-	Temperature programmed reduction
XRD	-	X-ray diffraction
ZSM-5	-	Zeolite Socony Mobil Five

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Natural gas may become more important both as an energy source and as the source of organic chemical feedstock in the 21st century (Javanmardi *et al.*, 2005). In 2001, natural gas accounted for a 24% share of the world's primary energy consumption (Aguiar *et al.*, 2005). In addition, economically recoverable natural gas reserves have risen continuously over the last decades. However, the world's natural gas reserves are located in only a few countries. The geographical distribution of natural gas is given in Figure 1.1. The largest reserves are located in the countries of the former Soviet Union and the Middle East. Future demands will be met by volumes from reserves located at even greater distances, and the investment associated with gas procurement is therefore expected to rise. Furthermore, the decline in oil production, which is forecast to occur from 2010-2020 onwards, will result in an increasing role for other fuels, most of which will be significantly more expensive (Ashman and Mullinger, 2005). Therefore, the evolution of the known natural gas reserves worldwide indicates a dramatic increase and this trend is expected to continue, which will, in addition to the price development with respect to the crude oil based upgrading-most likely generate a gradual shift towards the application of natural gas as a feedstock for the production of fuels and petrochemicals (Siddiq, 2002). This situation has forced an enhanced global interest in processes which can convert natural gas into liquids and higher added value products.

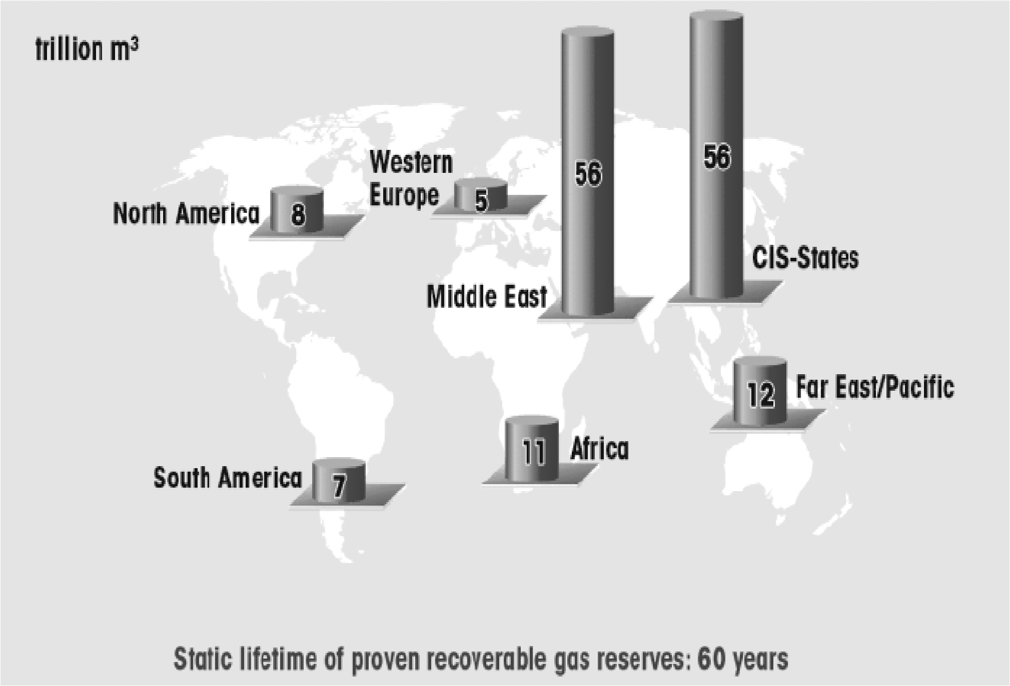

Figure 1.1 Geographical distribution of proven natural gas (*The BP Statistical Review of World Energy 2004*)

On the other hand, natural gas, which is basically methane, is a colourless, odourless fossil fuel that is already widely used in homes and industry, and will be used to a greater extent in the future. It is fairly inexpensive, clean-burning, and abundant, and in recent years, it has made headlines as a solution to many environmental and economic concerns facing this country. Because it has received so much positive attention, people are now looking at ways to increase our ability to recover and utilize this resource. Although it does have some drawbacks compared to other fuels, mainly issues dealing with its volume, it promises to be an increasingly important energy source in years to come.

Natural gas has shown to be a viable substitute for other fossil fuels, namely oil and coal, as concerns over the supply of these other nonrenewable fuels grow. Natural gas is also nonrenewable; however, we have large, untouched deposits in Malaysia that, if developed, will make the sale of natural gas easier in a recognized commodities market. Also, natural gas burns cleaner and produces less pollutant than other fossil fuels. It produces 45% less CO_2 than coal for a comparable amount of energy, and also emits considerably less nitrogen oxide and sulphuric acid

(Spivey, *et al.*, 2005). This is a good thing, because carbon dioxide has been blamed to be the cause of the 'greenhouse effect'.

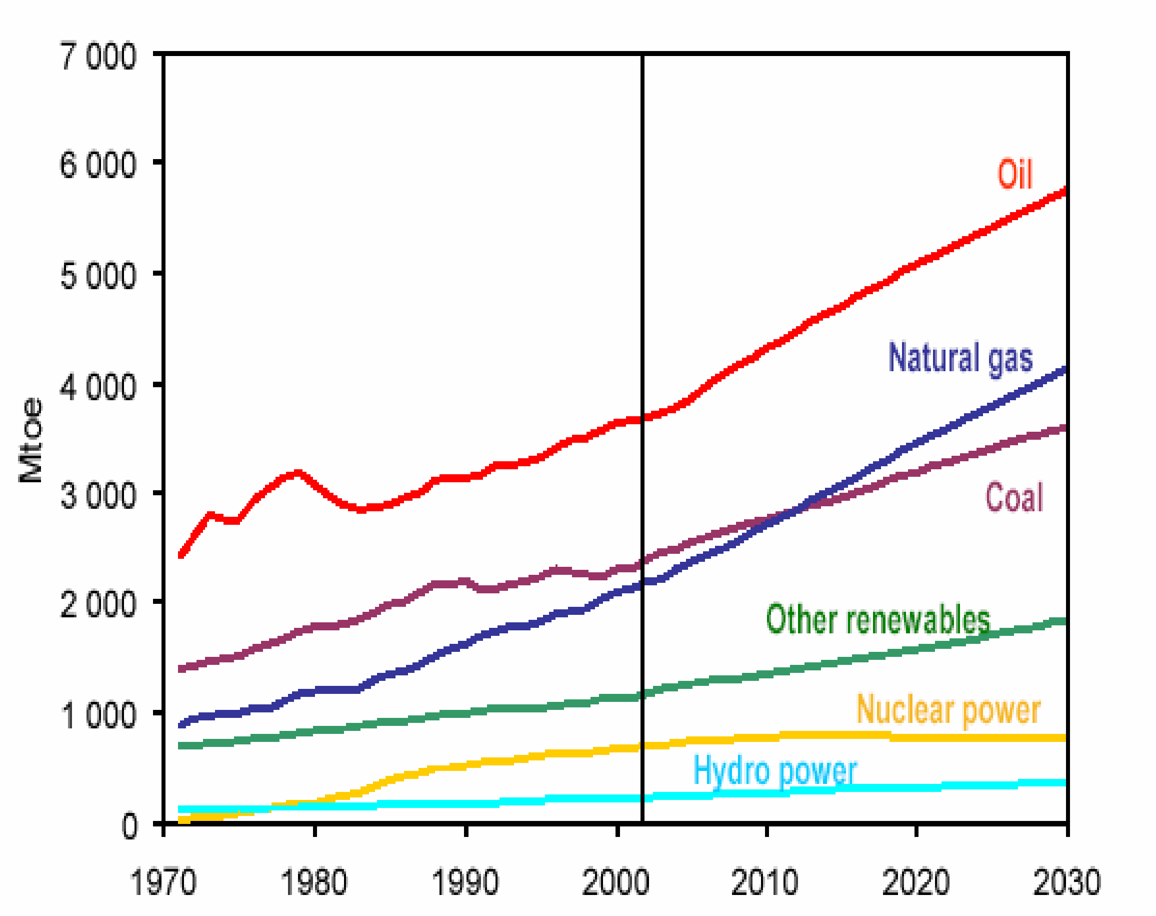

Figure 1.2 World Primary Energy Demand (Birol and Argiri, 1999)

Projections of world energy demand by fuel are illustrated in Figure 1.2. Oil continues to dominate world energy consumption. However, recent studies, based on the current energy consumption growth, have shown that the world petroleum reserve will be depleted within the next century (Lunsford, 2000). Thus, for the survival of the world, research on alternative feedstock utilization has become one of the prime technologies of the twenty first century and natural gas seems very promising at this stage. It burns with less emissions than gasoline, and has a higher fuel efficiency (a higher percentage of the energy in the fuel can be used). However, one concern with using natural gas is the volume of the gas, since it is much greater than that of liquid fuels. Even using CNG, (compressed natural gas), the fuel tanks of NGV's (natural gas vehicles) must be quite large, and even then, fuel range is not as much as if it had gasoline. On larger vehicles, such as buses, LNG (liquid natural gas) can be used. LNG is natural gas that is cooled to –166 degrees Farenheit, so that it condenses to a liquid (Kaneko *et al.*, 2004). Thus, it is much more dense than CNG, although still not as energy dense as gasoline or diesel. However, in order to use LNG, the vehicle must be equipped with a large cryogenic cooling system to keep the natural gas as a liquid, so LNG is not really feasible for smaller vehicles like cars.

Because the attention on natural gas as an alternative to oil or coal is relatively new, researchers are now working on ways to increase the production, processing, and distributing abilities of methane. As demand for natural gas rises in the future, probably sharply, a greater demand will be put on our natural gas infrastructure. When this occurs, a closer look will be directed to options that were previously thought unviable. Another area that is currently being developed in anticipation of the future demand is GTL (gas-to-liquid) technology. There are many potentially rich gas fields that are not drilled because of the need to lay expensive steel pipes to transport the gas. If the field is very far away from the storage reservoir, the cost of the pipeline could discourage any speculators on the field. Transporting by ship, train, or truck is much less costly, but methane's high volume as a gas prevents it from being transported in bulk. GTL is technology that allows the producer to convert the gas into a liquid fuel, allowing it to be transported much more compactly and hence more easily (Wilhelm *et al.*,2001). As mentioned before, liquid natural gas (LNG), is one way of accomplishing this.

However, the need to constantly keep LNG at a very low temperature is a drawback, sometimes a serious one. This leads to the other area of GTL, chemically reacting methane with other compounds, to produce a stable liquid methane-based fuel. This new liquid form is ready to be used for transportation, as well as to directly supply power to machinery, in the same manner gasoline is used. Producing GTL fuel is very costly at this time; however, because a methane-based liquid fuel has a large amount of positive characteristics, it is being heavily researched, and in the future, as costs go down, we should see more of these liquid hydrocarbon fuels.

1.2 Natural Gas

Natural gas is a combustible mixture of hydrocarbon gases. It is colorless, shapeless, and odorless in its pure form. As a safety measure, natural gas companies add an odorant, mercaptan, to the gas so that leaking gas can be detected. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely. Table 1.1 shows outlines the typical makeup of natural gas before it is refined. Natural gas is considered 'dry' when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is 'wet' (Thomas and Dawe, 2003).

The primary component of natural gas is methaneT (CH_4), the shortest and lightest hydrocarbon molecule. It may also contain heavier gaseous hydrocarbons such as ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), as well as other sulphur containing gases, in varying amounts, see also natural gas condensate. Organosulfur compounds and Hydrogen sulfide (H_2S see acid gas) are common contaminants, which must be removed prior to most uses. Gas with a significant amount of sulfur impurities is termed "sour". Moreover, combustion of one cubic meter of commercial quality natural gas yields 38 MJ (10.6 kWh) (Yagi *et al*., 2005).

Methane is also an extremely efficient greenhouse gas which may contribute to enhanced global warming when free in the atmosphere, and such free methane, would then be considered a pollutant rather than a useful energy resource. However, methane in the atmosphere reacts with ozone, producing carbon dioxide and water, so that the greenhouse effect of released methane is relatively short-lived. As a pollutant, significant biological sources of methane are termites, cattle (ruminants) and cultivation (estimated emissions are 15, 75 and 100 million tons per year respectively) (Aguiar *et al.,* 2005).

Natural gas is a fossil fuel like oil and coal, this means that it is, essentially, the remains of plants and animals and microorganisms that lived millions and millions of years ago. There are many different theories as to the origins of fossil fuels. The most widely accepted theory says that fossil fuels are formed when organic matter (such as the remains of a plant or animal) is compressed under the earth, at very high pressure for a very long time. This is referred to as thermogenic methane (Lunsford, 2000). Similar to the formation of oil, thermogenic methane is formed from organic particles that are covered in mud and other sediment.

Table 1.1 The typical composition of natural gas before it is refined (Kvenvolden, 1995)

Typical Composition of Natural Gas		
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	0-20%
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulphide	H_2S	0-5%
Rare Gases	A, He, Ne, Xe	trace

This sediment and debris puts a great deal of pressure on the organic matter, which compresses it. This compression, combined with high temperatures found deep underneath the earth, break down the carbon bonds in the organic matter. As one gets deeper and deeper under the earths crust, the temperature gets higher and higher (Lunsford, 2000). At low temperatures (shallower deposits), more oil is produced relative to natural gas. At higher temperatures, however, more natural gas is created, as opposed to oil.

1.3 Natural Gas Conversion Technologies

Natural gas is found in considerable amounts in oil fields, often at remote locations, where the construction of pipelines to transport the gas is not economical. Under these circumstances, it is usually flared, vented, or pumped undergrounds

(Thomas and Dawe, 2003). Therefore, finding an efficient process for utilizing such stranded gas receives considerable attention. In this direction, the conversion of methane, the main constituent of natural gas, into more valuable hydrocarbons is a topic of great interest. Up to now, indirect processes, involving partial oxidation and Fischer-Tropsch synthesis, are being used for this purpose. Recently many attempts have been made to develop a direct process for converting methane into higher hydrocarbons and the effective chemical activation of the methane molecule remains the most challenging step in such a process. In this research, an attempt is made to initiate a route for direct liquid hydrocarbons (C_{5+}) production by catalytic reaction oxidation of methane with oxygen. Before that, various technology of methane conversion to higher hydrocarbon will be discussed further in this chapter to obtain a complete understanding about the processes involved.

The abundance of natural gas (the main constituent of which is methane), together with steadily depleting oil reserves, highlights methane conversion to higher hydrocarbons as an extremely attractive goal. Activation of methane is very challenging due to its refractory nature and has made this one of the most extensively investigated processes in catalysis. The processes of conversion of natural gas into liquid higher hydrocarbons products can be divided into two types: direct conversion and indirect conversion as shown in Figure 1.3. The primary step of the indirect route involves the production of syn-gas (a mixture of CO and H_2) by steam reforming, partial oxidation, autothermal reforming; following this step the syn-gas is converted to hydrocarbons directly via Fischer–Tropsch catalysis or indirectly via other intermediates such as methanol.

The direct conversion processes utilize catalysts and specific synthesis routes to chemically transform the molecules of methane, the main component of natural gas, into more complex chained substances with heavier molecules. The desired products that can be obtained include the alcohols (mainly methanol), the olefins (ethylene and acetylene) and the aromatics (benzene, toluene and naphthalene). However, the high stability of the methane molecule creates a series of technical problems to make the chemical reactions involved viable. Thus, the research and development efforts of the direct conversion processes are focused on the improvement of the catalysts in the elucidation of the mechanisms of reaction and the development of new equipment.

Taylor *et al.* (1988) explained that methane, oxygen, and hydrogen chloride (mixed CuCI, KCI, $LaCI_3$) are reacted over an oxyhydrochlorination catalysts. In the first stage produce methyl chloride and water. In second stage, the methyl chloride is converted to higher hydrocarbons, namely paraffins, olefins, aromatics and cycloparaffins, over zeolite, such ZSM-5, as shown by the chemical equation in (Equation 1.1 and Equation 1.2).

$$CH_4 + O_2 + HCI \xrightarrow{CuCl,\ KCl,\ LaCl_3} CH_3CI + H_2O \tag{1.1}$$

$$CH_3Cl \xrightarrow{ZSM\text{-}5} \text{Gasoline} + HCI \tag{1.2}$$

They reported that the conversion of methlychloride to gasoline range hydrocarbon (31-42 %) accurse under conditions similar to those for methanol to gasoline conversion. The oxyhydrochlorination catalysts was prepared in a non-aqueous solvent by successive impregnation of metal chloride salts onto a silica support. Final weight composition was as 41.7 % CuCI, 37.5% SiO_2, 11.5 % KCI and 9.4 % $LaCI_3$. the ZSM-% catalysts was obtained from Mobil Oil Cooperation in the ammonium form with silica to alumina ratio of 70:1 (Tylor *et al.*,1991). The ammonium form was converted to the hydrogen form by calcaning in air at 538 ^{o}C for 16 hrs.

Senkan (1987) has patent a process for oxidative pyrolysis of halogenated methanes in the gas phase and under non-flame conditions in the presence of oxygen which significantly reduces the formation of carbonaceous deposits, such as tars, solid carbon and soot, while maintaining high yields, in the order of 20 to 80 percent, of desired higher molecular weight hydrocarbon products. According to a preferred embodiment, the process of that invention may be a two step process wherein the first step involves the halogenation of methane using a halogen containing gas or oxyhalogenation using hydrogen halide in the presence of oxygen. Then in a second step, the halogenated methanes are oxidatively pyrolyzed under non-flame conditions in the presence of an oxygen containing gas. The process of that invention may also be a single step process wherein the methane halogenation and the oxidative pyrolysis of halogenated methanes are accomplished in a single vessel. According to that invention, oxygen converts to carbon monoxide hydrocarbon compounds which would otherwise result in the formation of carbonaceous deposits during conversion of halogenated methanes. Oxidative pyrolysis of the halogenated methanes yields higher molecular weight hydrocarbons such as acetylene and ethylene.

A process for oxidative pyrolysis of halogenated methanes in the presence of oxygen-containing gas under non-flame conditions is provided whereby the formation of solid carbonaceous materials is significantly reduced, while high yields of desired higher molecular weight hydrocarbons such as acetylene and ethylene are maintained. However, the oxyhydrochlorination process is not economical, because the chloride acid is very corrosive and the cost of special materials were replaced with carbon steel throughout (Cavani and Trifiro, 1997).

The indirect route is technically easier than that of the direct conversion processes. The technologies of the processes involved have been better studied and several pilot and commercial plants are already in operation (Wilhelm, 2001). The processes of indirect conversion are characterized by a preliminary stage of transformation of natural gas into synthesis gas - syngas - (a mixture of carbon monoxide - CO and hydrogen - H_2). Synthesis gas production requires either steam (steam reforming) or oxygen (partial oxidation) as a co-reactant. In either case, generation of these reactants is extremely energy and capital intensive and, as a result, the major cost of converting natural gas to liquid fuels lies in the initial synthesis gas production step. After being produced, the syngas is converted into liquid hydrocarbons through the Fischer-Trospch Process (FT) (Gradassi and Green, 1995; and Vosloo, 2001).

On the other hand, hydrogen is perceived as an ideal energy carrier for a clean and sustainable energy future in the world, and fuel cells will play a significant role in this hydrogen based energy system as flexible, clean, and efficient energy devices suitable for use in a wide range of transportation and stationary/portable power generation applications. Among many potential sources for hydrogen

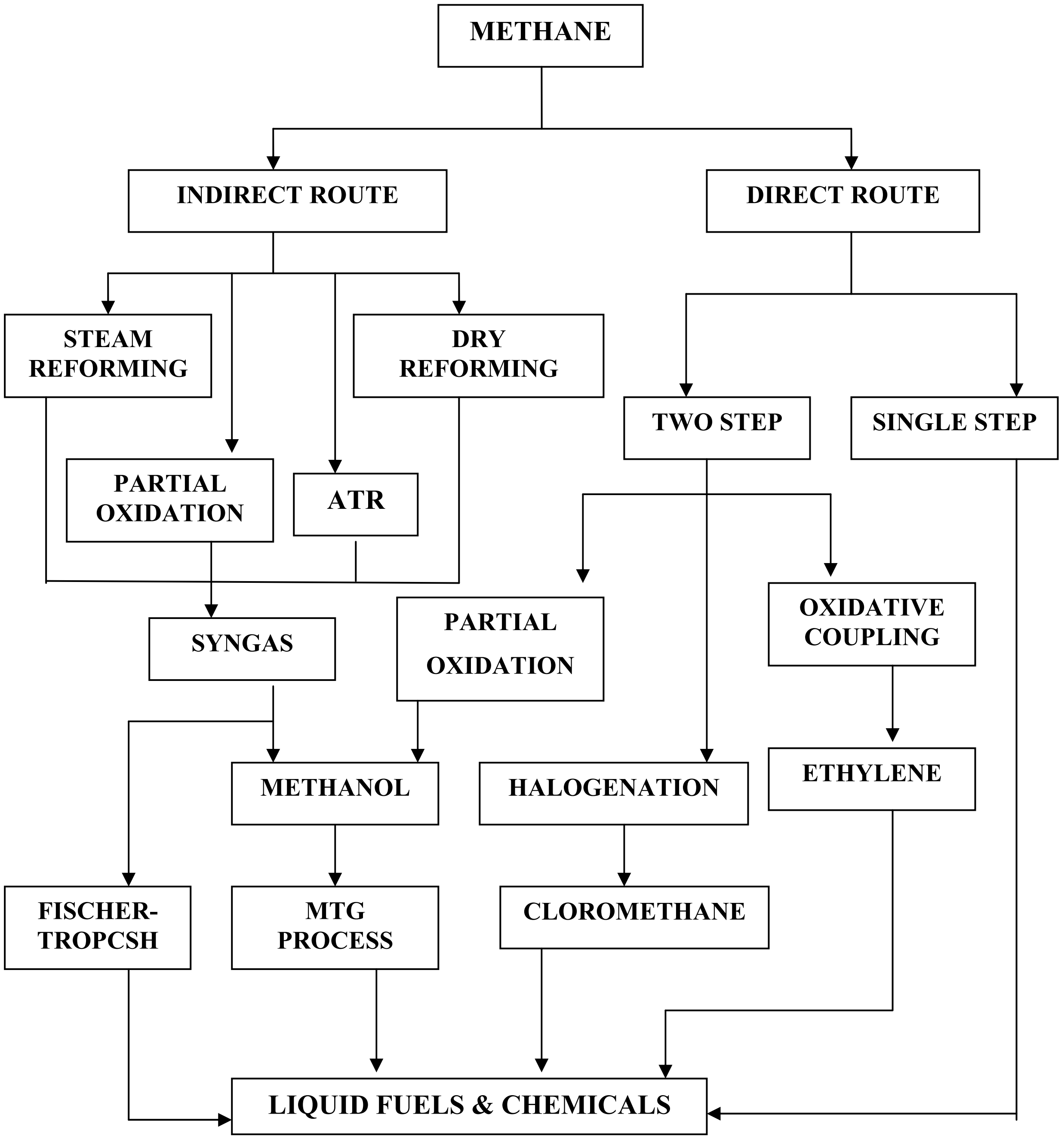

Figure 1.3 Methane to liquid hydrocarbons conversion routes

generation, natural gas, which is clean hydrocarbon fuel, abundant, and well-distributed, is considered to be one of the ideal fuels for hydrogen source for fuel-cell stationary applications. Many companies are developing natural-gas fuel-cell systems for residential/stationary applications and commercial/industrial markets. Reforming natural gas is a well-established technology in the petrochemical and fertilizer industries for the production of hydrogen for use in the manufacture of ammonia, methanol, and other chemical products (Lee *et al.*, 2005) This technology has been reviewed in detail and includes three basic processes: steam reforming (SR), partial oxidation reforming (POR), and auto thermal reforming (ATR). In recent years, the catalytic ATR process has received much research and development attention as a viable process for hydrogen generation for fuel-cell systems because it offers advantages of simpler design (smaller and lighter unit), lower operating temperature (easier start-up and a wider choice of materials), and flexible load following characteristic as compared to the SR process. It also has higher energy efficiency than the POR process (Lee *et al.*, 2005).

The methane-steam reforming reactions are strongly endothermic and the thermodynamic equilibrium is favored by high temperature. The conventional steam reformers are mainly fixed bed catalytic reactors. The catalyst is normally loaded into a number of tubes placed in a furnace, which operates at high temperature varying from 850 to 1100 K. The reactors suffer from uniform distribution of heat fluxes and profound effect of high temperature on the tubes and catalyst life. Moreover, the diffusion limitations are severe with very low effectiveness factor in the order of (10^{-2}–10^{-3}) (Abashar, 2004). In addition, the reactions produce significant quantities of carbon dioxide (important greenhouse gas), which is harmful to the environment.

In recent years various experimental and theoretical attempts have been made to improve different aspects of processing methane to produce hydrogen. Considerable attention has been paid to the fluidized bed membrane reactors (FBMRs) as multi-functional reactors (Abashar, 2004). Their main advantages are: shift of the thermodynamic equilibrium, enhancement of methane conversion, simultaneous reaction and separation of hydrogen, elimination of diffusion limitations, good heat transfer capability and a more compact design (Laosiripojana and Assabumrungrat, 2005). Also, the carbon dioxide reforming of methane, the so-called dry reforming of methane (CO_2 reforming) has gained increasing importance. The process of great significance for environmental protection, it enables the transformation of CO_2 into synthesis gas (syngas). Recently, several studies have shown that the performance of the fixed bed catalytic reactors has improved significantly by introduction of the dual-functionality via structured pattern (either mixed or layered configuration) of the catalyst bed. The purpose of these patterns is to couple the reactions in different ways to achieve certain degree of integration of heat, further shift of thermodynamic equilibrium and simultaneous production of more than one product (Abashar, 2004).

The following sub-chapters will deal with the ‘‘GTL’’- technology as well as the oxidative coupling of methane (OCM), where zeolites and related MgO based material respectively have been demonstrated to be superior catalysts.

1.3.1 Gas to Liquids (GTL) Technology

GTL technology is based on the conversion of natural gas to liquid fuels in three stages: synthesis gas generation, production of heavy-chain hydrocarbons by Fischer-Tropsch synthesis and heavy fraction hydrocracking for production of useful compounds such as naphtha, diesel and lubricants (Figure 1.4) (Aguiar *et al.*, 2005; and Yagi *et al.,* 2005). Although the three stages of the GTL process by indirect means have been individually well studied and are available for commercialisation, an optimal combination that permits the reductions of costs of the commercial production plants still does not exist. Additionally, the synthesis gas generation stage corresponds to the greatest costs in investments and operation, being responsible for around 50–75% of the capital costs (Vosloo, 2001). Therefore, many large companies are seeking to optimize the synthesis gas generation stage, in order to make the GTL technology commercially viable (Wittcoff *et al.,* 2004).

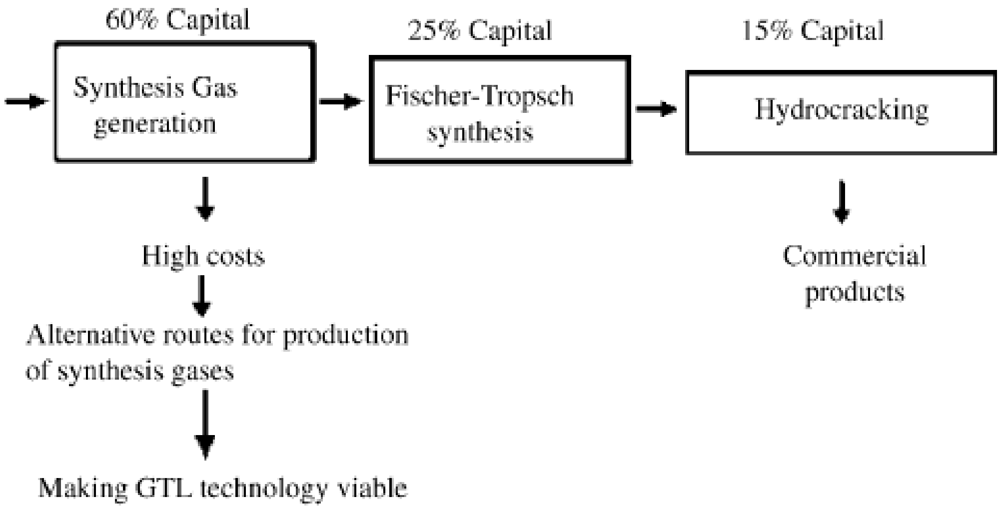

Figure 1.4 Typical stages in GTL technology (Yagi *et al.,* 2005)

On the other hand, fuels production directly from syngas (in former times obtained from coal) has been reported by Fischer and Tropsch in 1923 for the first time (Wilhelm *et al.*, 2001), using an alkali-promoted iron catalyst. Fuels manufactured via the Fischer–Tropsch route reveal an excellent quality since they consist mainly of linear paraffins and olefins and do not contain sulfur and aromatics. A Co-containing catalyst is applied for the production of heavy paraffins via the Fischer–Tropsch route starting with natural gas, a technology developed by Shell and named the ‘‘Shell Middle Distillate Synthesis (SMDS)’’ route (Lunsford, 2000). In addition, diesel fuel (or gasoline) is produced by hydrocracking of the more or less sulfur and nitrogen-free wax obtained through the SMDS process using noble metal containing zeolites. The more restricted fuel specifications currently introduced in order to reduce the environmental impact of hazardous emissions represent a driving force with respect to an increased use of fuels prepared via the Fischer–Tropsch route as a blending component of the gasoline and diesel pools in the future (Aguiar *et al.*, 2005). Figure 1.5 is a block flow diagram of the GTL process.

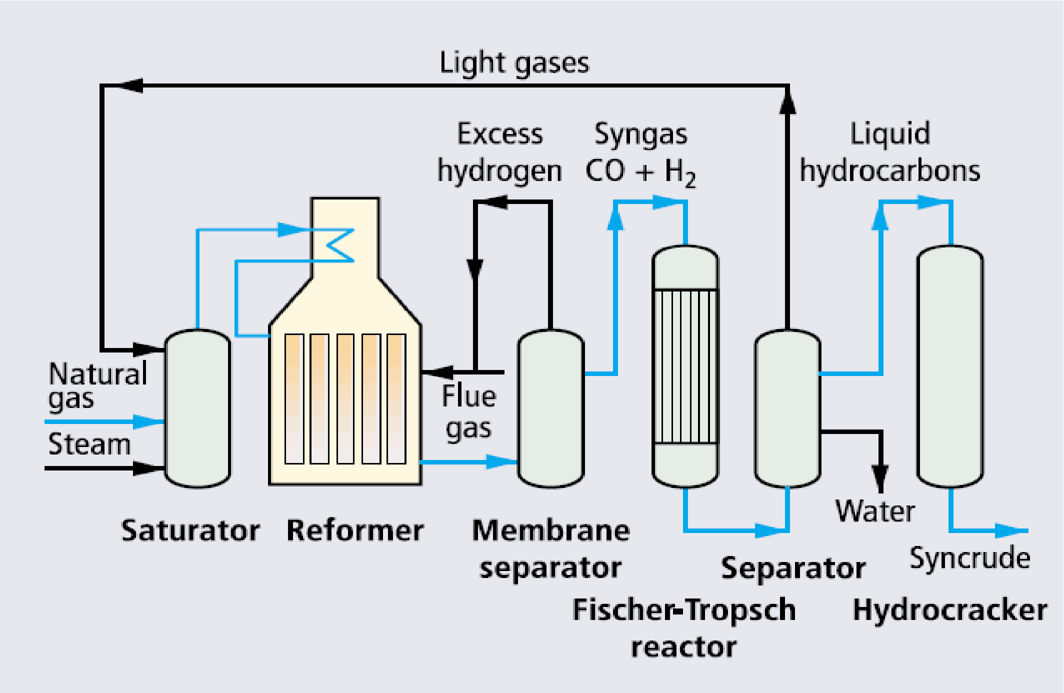

Figure 1.5 Flow diagram of the GTL process (Aguiar *et al.*, 2005)

Besides the SMDS technology, an alternative has been presented by SASOL/Chevron termed as the ‘‘Slurry-Phase-Distillate’’ process, again based on the Fischer–Tropsch route producing wax (using a Co-containing catalyst) followed by a hydrocracking step in order to get diesel or gasoline (Espinoza *et al.*, 1999). The methanol to gasoline (MTG) plant in New Zealand has been combined with a methane steam reforming unit for production of synthesis gas and a methanol plant to produce gasoline from natural gas. The process economics can be improved considerably by a clever combination and close integration of the different steps. Finally, ExxonMobil has introduced the so-called ‘‘Advanced Gas Conversion for the 21st Century’’ (AGC-21) technology, again based on the Fischer–Tropsch route (Ashley *et al.,* 2003; and Wittcoff, *et al.,* 2004).

In any manner, the reduction of costs of any stage is still the principal objective of all companies developing GTL. The use of catalytic membranes and compact reformers represents considerable advances in the area. Another possibility is in the elimination of the isomerization unit, which would occur if the Fischer–Tropsch catalysts were able to generate isomerized products. The addition of

Bronsted acid sites to the traditional cobalt catalysts appears to be an interesting research option that is still under-explored. This catalyst was tested and refined to improve performance; thus creating an ultra-stable catalyst with high activity and selectivity. Using an integrated simulation model for reforming and F-T synthesis, designers developed detailed mass balance flowsheets, engineering line diagrams, utility line diagrams, plant layouts, process and mechanical specifications of all equipment and instrumentation and comprehensive schedules of all bulk materials.

1.3.2 Oxidative Coupling of Methane

Conversion of methane into liquid products is traditionally achieved via steam reforming to produce CO and H_2, followed by transformation of these diatomic molecules into oxygenates and higher hydrocarbons. Because the energy input required for steam reformation is exorbitant, alternative routes to methane conversion have been pursued. One approach which leads to direct formation of C_2 products is oxidative coupling of methane (OCM).

This oxidative coupling of methane (OCM) is a promising route for the conversion of natural gas to ethylene that can be used for the production of petrochemicals or fuel. The reaction takes place in the presence of catalysts at temperatures from 650 to 850^{o}C (Zaman, 1997). In the oxidative coupling reaction, CH_4 and O_2 react over a catalyst at elevated temperatures to form C_2H_6 as a primary product and C_2H_4 as a secondary product. The reaction network is interesting from a fundamental perspective because it is an example of a heterogeneous–homogeneous system.

Oxides of alkali, alkaline earth and rare earth metals, singly or in combination, catalyze the reaction to the desired path. Maitra (1993) analyzed the performance of the different types of OCM catalysts and concluded that only the basic oxides constitute good catalysts. According to this mechanism, the methane activation proceeds via hydrogen abstraction on a basic O^{2-} site producing CH^{-}_3 which, in a secondary reaction with oxygen, produces $CH_3\cdot$, simultaneously converting O_2 to O^-_2. Methyl radicals that are formed at the surface of the catalyst enter the gas phase where they couple to form ethane. Over basic oxides catalysts, it is indeed observed that secondary reactions of ethane are responsible for ethylene formation (Martin and Mirodatos, 1995).

In addition to coupling, the gas phase radicals may enter into chain reactions that result in the formation of CO and subsequently CO_2. Isotopic labeling experiments have demonstrated that at small conversion levels, most of the CO_2 is derived from CH_4, but at commercially significant conversion levels, C_2H_4 would be the dominant source of CO_2 (Martin and Mirodatos, 1995). Additional experiments have shown that this occurs mainly via a heterogeneous reaction. One of the challenges in catalyst development is to modify a material so that the secondary reaction of C_2H_4 will be inhibited while the activation of CH_4 will still occur. There is no inherent reason that these two reactions should take place on the same types of sites. A complex model of the OCM reaction over a lanthanum basic oxides catalyst is summarized in Figure 1.6 (Mleczko *et al.*, 1995).

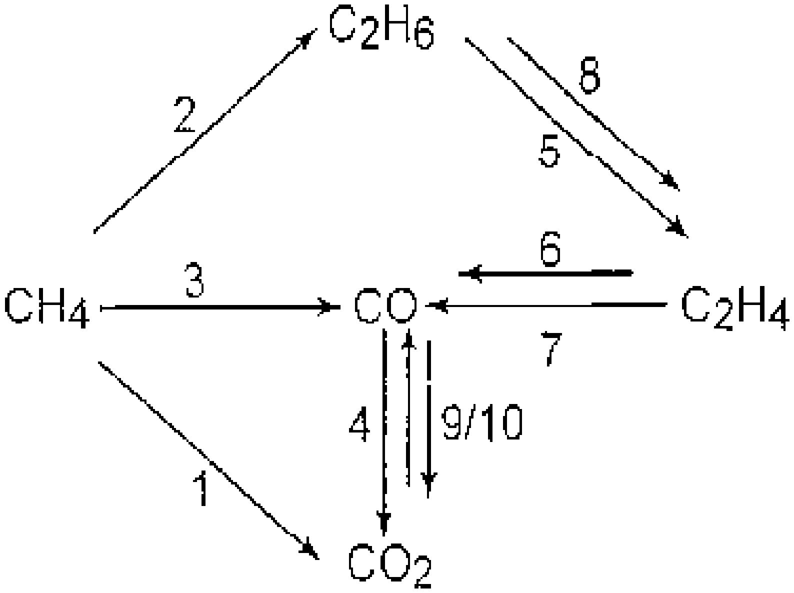

Figure 1.6 Reaction scheme of the OCM over the basic oxides catalyst (Mleczko *et al.*, 1995)

The scheme includes the nine heterogeneously catalyzed and one homogeneous non-catalytic (reaction 8) reactions:

(1) total oxidation of methane to carbon dioxide,
(2) oxidative coupling of methane to ethane,
(3) partial oxidation of methane to carbon monoxide,
(4) oxidation of carbon monoxide to carbon dioxide,
(5) oxidative dehydrogenation of ethane to ethylene,
(6) oxidation of ethylene to carbon monoxide,
(7) steam reforming of ethylene,
(8) thermal dehydrogenation of ethane to ethylene,
(9/10) conversion of CO to CO_2 and vice versa

1.3.3 Hydrogen from Methane Conversion Reaction

Hydrogen is used as both a chemical feed and a fuel, and is generally produced by steam reforming of hydrocarbons, especially natural gas, from water gas shift reactions, from catalytic reforming of petroleum stocks and by electrolysis. It has been reported that hydrogen can be formed by the decomposition of methane over iron catalysts. This process results in the formation of coke on the catalyst, which ultimately destroys the activity of the catalyst. It may be assumed that decomposition of methane produces hydrogen and carbon black by the following single reaction (Cho *et al.*, 2004):

$$CH_4 + 75.3\ (\mathrm{kJ/mol}) \rightarrow C + 2H_2 \quad (1.3)$$

According also to Cho *et al.* (2004), the total enthalpy of methane decomposition at 1873 ^{0}C is 182.7 kJ/mol, and the energy related to carbon mass varies approximately between 4 and 7 kW h per kg of carbon produced or 1 and 1.9 kW h per normal cubic meter of hydrogen produced.

In the case of OCM and oxidative dehydrogenation (ODH) it is very likely that a serious problem will be faced when trying to extract the intrinsic kinetic constants of elementary heterogeneous interactions from experimental data. The rates of reactant conversion and product formation are a complex combination of terms attributed to numerous elementary reactions localized both on the catalyst surface and in the gas phase. However, such a conversion is highly endothermic; under the high temperature reaction conditions required therefore, control of the reaction to prevent the formation of unwanted by products is difficult.

As Sinev *et a*l.(2003) demonstrated earlier, free-radical gas-phase processes play a very important role in product formation during light alkane oxidation. The development of chain process in the gas phase leads to the formation of various radical and molecular species further transformations of which can produce hydrogen. First of all, alkyl radicals C_nH_{2n+1} formed as primary radical species during alkane activation in heterogeneous or homogeneous steps can undergo consecutive scission evolving H-atom which then reacts with any H-containing molecules RH (first of all, with initial alkane) with H_2 molecule formation:

$$[O]_S + C_nH_{2n+2} \rightarrow [OH]_S + C_nH_{2n+1} \quad (1.4)$$

$$X + C_nH_{2n+2} \rightarrow XH + C_nH_{2n+1} \quad (1.5)$$

$$C_nH_{2n+1} \rightarrow H + C_nH_{2n} \quad (1.6)$$

$$RH + H \rightarrow R + H_2 \quad (1.7)$$

where $[O]_S$ is the active surface site; X is any gas particle which has an affinity to hydrogen atom (e.g. O_2, OH, HO_2, H, alkyl, alkoxy, alkylperoxy species, etc.).

As can be seen, the sequence of steps (1.4), (1.6) and (1.7) leading to the formation of at least one olefin and one H_2 molecules and to the development of homogeneous chain process starts from the oxidative abstraction of H-atom from alkane molecule by a surface active site. If a chain initiation takes place in the gas phase, the first step (3) (in this case $X = O_2$) is also an oxidative H-atom abstraction. The same can be said about alkane molecule reaction (1.5) with any oxidative particles present in the gas phase during a developed chain reaction. In other words, this sequence of steps can be considered as an oxidative process leading to molecular hydrogen forming in parallel with olefin. In the work dedicated to the OCM process, Sinev (2003) explained the formation of high concentrations of molecular hydrogen during methane oxidation at moderate temperatures (below 650 °C) by the formation and rapid decomposition of formaldehyde.

The overall reaction of oxidative coupling is:

$$4CH_4 + O_2 \rightarrow 2\ C_2H_6 + 2H_2O \tag{1.8}$$

followed by dehydrogenation of ethane to ethylene:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{1.9}$$

However the detailed reaction mechanism is very complex. The many possible side reactions produce other oxidation products such as CO and CO_2. Although hydrogen is also a product of the OCM reaction, it is normally converted back to other products via complex reaction mechanism.

In the conditions of optimal production of olefins during oxidation of light alkanes over typical OCM catalysts molecular hydrogen forms as one of the major products. Variations of kinetic features depending on the initial alkane, catalyst and reaction conditions are indicative for the existence of multiple pathways of hydrogen formation. If almost total conversion of oxygen takes place in the front part of the reactor, non-oxidative dehydrogenation (NODH) process can proceed in the remaining part of catalyst bed. Over some catalysts hydrogen formation can also accompany the intense coking. In addition to non-oxidative routes, some oxidative processes, including those proceeding in the gas phase, can lead to the production of hydrogen which in this case is accompanied by both additional olefin formation and total oxidation. However, reactions followed by the hydrogen oxidation by oxygen and hydrogenation with primarily formed olefins decreased the yield of hydrogen in the OCM final reaction products. Further elucidation of the reaction pathways can help to improve the target olefin production in the OCM reaction.

On the other hand, oxidative dehydrogenation (ODH) of light alkanes attracts a considerable attention as a potentially efficient way to produce olefins from relatively cheap and abundant feedstocks. The main usually discussed advantage of

ODH over NODH of the same alkanes is the absence of thermodynamic limitations for per-pass olefin production since in the case of NODH an upper limit of yield determined by equilibrium cannot be exceeded. The thermodynamics of CH_4 conversion is shown in Figure 1.7. Coke formation by reaction (1) in (Figure1.7) is most favorable, it can become one of the steps whereby supported noble metal catalysts can be inactivated.

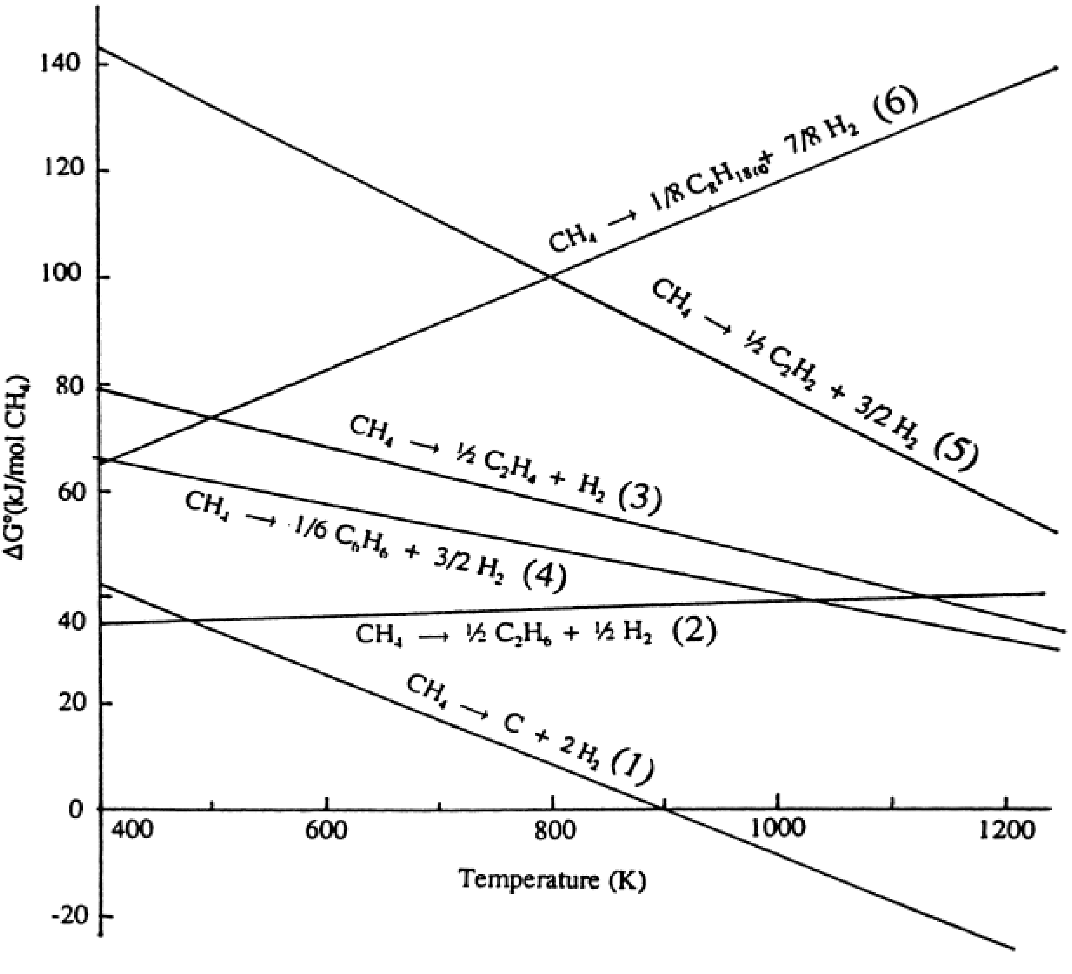

Figure 1.7 Thermodynamics of some methane conversion reactions which produce hydrogen (Gesser and Hunter, 1998)

In principle, the removal of hydrogen from the reaction system by any means helps to eliminate the thermodynamic limitations for olefin formation. For instance, selective in situ burning of hydrogen formed over NODH catalyst enables to increase olefin yields. However, catalytic ODH is considered as the most promising way to avoid thermodynamic limitations and necessity of external heating during the production of olefins from light alkanes. Indeed, if oxidant (e.g. molecular oxygen) is added to the feed gas the process becomes thermodynamically favorable at any level of alkane conversion and olefin yield. The only condition which has to be provided is water formation instead of H_2.

In real practice, however, neither water, nor hydrogen are usually measured experimentally when the reaction mixture is analyzed by on-line gas chromatography (GC). An accurate analysis of water requires additional complications of sampling system. As to the GC analysis of molecular hydrogen, some problems are discussed below. As a result, the analysis of experimental sections of publications dealing with ODH of light alkanes shows that in most cases in these studies only carbon balance is a subject of concern and the fate of hydrogen abstracted from alkane molecule cannot be traced because neither H_2, nor water are analyzed. On the other hand, it is well known that substantial amount of hydrogen are formed during the oxidative coupling of methane (OCM) which is relative to ODH process (both reactions require elevated temperatures; they both proceed via the abstraction of H-atom from C–H bond; OCM catalysts are very efficient in ODH). The detailed studies of hydrogen formation during oxidation of C_1–C_4 alkanes over a series of typical ODH catalysts undertaken in some OCM works indicates that the reaction pathways are much more complicated than it has been believed previously. However, the analysis of product yields shows that even if NODH is the only process leading to the formation of olefin, hydrogen production exceeds by far the value corresponding to the formation of olefin and its possible sequential overoxidation. This indicates that certain pathways of hydrogen formation become more important at increasing length of carbon chain in hydrocarbon molecules. The trends described above are suggestive for an existence of multiple pathways for hydrogen formation in the conditions of alkane oxidation in OCM reactions. These pathways should follow different kinetic regularities when reaction parameters, such as temperature, residence times and reactant concentrations, are varied.

Moreover, since the highest concentrations of hydrogen in the reaction mixture are observed in the conditions close to optimal olefin formation, the elucidation of the process pathways is worth for further optimization of target product yield. In fact, one possibility is that a substantial fraction of olefin forms simultaneously with H_2 via NODH over reduced catalyst at the expense of heat produced in total oxidation reaction (in which the most part of oxygen is consumed). If so, there is no practical reason to run the reaction in the oxidative mode and a more economical way to supply heat for NODH should be found. On the other hand, if hydrogen formation is a result of some by-processes, special efforts should be mounted to suppress them. In the latter case, monitoring of H_2 concentration in the reaction mixture is a good way to control the efficiency of these efforts.

Under the usual reaction conditions for the OCM, H_2 is a major reaction product although early studies failed to observe or seemed to have overlooked this due to analytical difficulties, as mentioned in above. Therefore, not many studies seem to have reported the production of H_2 among the numerous studies on the OCM (Choudhary *et al.*, 1997 and Lacombe *et al.*,1994). H_2 can be formed via a number of pathways, such as steam reforming reactions, the water-gas shift reaction, homogeneous gas-phase methane oxidation, and decomposition of ethyl radicals (Heracleous and Lemonidou, 2004). From a detailed study on the OCM over MgO, Hargreaves *et al.* (2002) have reported that the water-gas shift reaction is an important H_2 source and that partial oxidation of hydrocarbons becomes more significant at high flow rates and low O_2 conversions; also involved is thermal cracking of ethane to ethene. Hutchings *et al.* (2002) have proposed from a study on the OCM over MgO, La_2O_3 and Sm_2O_3 that gas-phase radical oxidation which is linked directly to the formation of carbon oxides is important but dehydrogenation of ethane is discounted as a major route due to the thermodynamic limitation. Possible reactions producing H_2 in the OCM process are listed as follows (Hong and Yoon, 2001):

Steam reforming of hydrocarbons:

$$CH_4 + H_2O = CO + 3H_2;\ H_2 : CO = 3 \qquad (1.10)$$

$$C_2H_6 + 2H_2O = 2CO + 5H_2;\ H_2 : CO = 2{:}5 \qquad (1.11)$$

$$C_2H_4 + 2H_2O = 2CO + 4H_2;\ H_2 : CO = 2 \qquad (1.12)$$

Partial oxidation of hydrocarbons:

$$CH_4 + 1/2O_2 = CO + 2H_2; \ H_2 : CO = 2 \qquad (1.13)$$

$$C_2H_6 + O_2 = 2CO + 3H_2; \ H_2 : CO = 1{:}5 \qquad (1.14)$$

$$C_2H_4 + O_2 = 2CO + 2H_2; \ H_2 : CO = 1 \qquad (1.15)$$

CO_2 reforming of hydrocarbons:

$$CH_4 + CO_2 = 2CO + 2H_2; \ H_2 : CO = 1 \qquad (1.16)$$

$$C_2H_6 + 2CO_2 = 4CO + 3H_2; \ H_2 : CO = 0{:}75 \qquad (1.17)$$

$$C_2H_4 + 2CO_2 = 4CO + 2H_2; \ H_2 : CO = 0{:}5 \qquad (1.18)$$

Water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \qquad (1.19)$$

In summary, it is proposed that the major pathways for the production of H_2 over the OCM catalysts are the dehydrogenation of ethane, steam reforming and partial oxidation of ethane and ethene which accompany simultaneous production of CO.

1.4 Heterogeneous Catalysis and Catalyst

A catalyst is a substance which controls the rate of reaction without itself undergoing a permanent chemical change and the process is called catalysis. The modern concept of catalysis was defined by Berzelius as follows: "Catalysis is a process whereby a reaction occurs faster than the uncatalyzed reaction, the reaction being accelerated by the presence of a catalyst" (Krische, 2005; Somorjai and McCrea, 2000; Haller, 2003; and Ponec, 1998).

There are two types catalyst, which are positive catalyst and negative catalyst or inhibitor. A positive catalyst increases the rate of reaction by lowering the energy of activation. Thus, in the presence of a positive catalyst, the greater fraction of the total molecule will posses lower energy of activation and collided successfully in a short period of time, there by increasing the rate of reaction. A positive catalyst functions by providing an alternate path to the reaction or by the formation of a transition (intermediate) compound having low energy of activation as shown in Figure 1.8. The activation energy of this path is lower. As a result the rate of reaction is increased. A negative catalyst retards the rate of reaction. A negative catalyst does not lower the energy of activation; rather it is combined with reactant molecule thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence the rate of reaction (Fogler, 1999).

Catalysis can be classified as homogeneous catalysis, in which only one phase is involved, and heterogeneous catalysis, in which the reaction occurs at or near an interface between phases (Bond, 2000; and Chen *et al.*, 2005a). The choice for a certain catalyst for a catalytic conversion is not only determined by the reaction itself but also by the industrial process (Taguchi and Schuth, 2005). For example, heterogeneous catalysts are used for the production of bulk chemicals because the solid catalyst materials are unmixable with products. This facilitates the separation of products and catalyst material, especially if gaseous products are involved. Consequently, the reaction can be performed under continuous flow conditions which permits the scaling up of production processes to achieve high rates. This advantage of heterogeneous catalysis is of exceptional importance because it allows the production of gasoline, fuel oil and other bulk chemicals on a large scale which is essential to provide sufficient bulk chemicals to satisfy the vast demands of the world market (Holzwarth *et al.*, 2001; Blaser, 2000; and Kerby *et al.*, 2005). Because most of the work presented in this thesis focuses on zeolite material and MgO based OCM catalyst, a brief description of these catalysts is presented in the next sections.

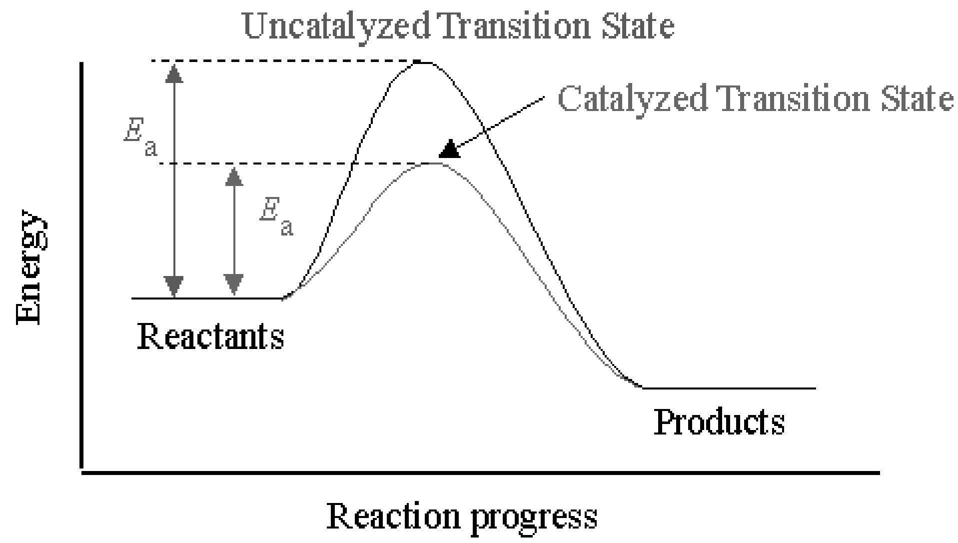

Figure 1.8 A catalyst provides an alternative route for the reaction with a lower activation energy (Somorjai and McCrea, 2000)

1.4.1 Zeolite

1.4.1.1 History and Zeolite Development

The word "Zeolite" was first used by a Swedish mineralogist Axel Cronstedt. In 1756, he discovered the very first zeolite mineral "stilbite". This mineral visibly lost water when heated. Accordingly, he named this class of mineral "zeolite" from the classical Greek words "zeo", meaning to boil, and "lithos", meaning stone. Since then, about 40 different kinds of natural zeolites have been identified (Erdem *et al.*, 2004). They vary in crystal structure and chemical composition, and some physical properties as well. Today, most natural zeolites have been successfully synthesized in laboratories or in commercial plants. Besides natural zeolites, man-made or synthetic zeolites have also added many new members to the zeolite family. Scientists have synthesized many zeolites that do not exist naturally or at least have not been discovered on the earth (Casci, 2005).

Zeolite is defined by Smith (1963) as "an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration"(Murakami *et al.,* 1986). Other definitions can also be found. Jacobs (1977) gave the following definition: "Zeolites as synthesized or formed in nature are crystalline, hydrated alumino-silicates of group I and II elements. Structurally, they comprise a framework based on an infinitely extending three-dimensional network of SiO_4 and AlO_4 tetrahedra linked together through common oxygen atoms" (Jeanette, 1980). Szostak (1989) stated that "structurally, zeolite is a crystalline aluminosilicate with a framework based on an extensive threedimensional network of oxygen ions"(Ribeiro *et al.*, 1995). Recently, Corma (2003) defined zeolite as "crystalline silicalites and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions." Although the four definitions are stated differently, the main characteristics of a zeolite are either clearly expressed or implied as a crystalline material of aluminosilicate featured by a three-dimensional microporous framework structure built of the primary SiO_4 and AlO_4 tetrahedra, and ion-exchange capability.

Nowadays, zeolites are available on a large scale and in a variety of applications. The major use of zeolites is as ion exchangers in laundry detergents where they remove calcium and magnesium from water by exchanging it for sodium present in the zeolite. Furthermore, zeolites are applied as adsorbents in the purification of gas streams to remove water and volatile organic species, and in the separation of different isomers and gas-mixtures. Moreover they are applied in the clean up of radioactive wastes. However, in this thesis the focus will entirely be on the application of zeolites as catalysts for the conversion of hydrocarbons. Catalysis by zeolites with focus on hydrocarbon conversion and formation covers, nowadays, a broad range of processes related to the upgrading of crude oil and natural gas. This includes, among others, fluid catalytic cracking (FCC), hydrocracking, dewaxing, aliphate alkylation, isomerisation, oligomerisation, transformation of aromatics, transalkylation, hydrodecyclisation as well as the conversion of methanol to hydrocarbons (Stocker, 2005). All these conversions are catalyzed by zeolites or related microporous materials, based both on the acid properties and shape-selective behavior of this type of materials.

The ordered, crystalline structures imply that the micropores in zeolites have very well-defined dimensions and connectivities. In addition, the framework composition can be tuned to enhance chemical selectivity. These features combine to ensure that zeolites form a very important category of cheap, highly reproducible size and shape selective molecular sieves and adsorbents which find widespread use in industry (Weitkamp, 2000).

Moreover, as extensively used porous materials, zeolites show marked advantages over other solid materials (Stocker, 2005; and Corma, 2003):

- ✓ Well defined structure which could be clearly related to the activity and selectivity;
- ✓ Well defined inner pores in which active species can be hosted;
- ✓ Adjustable frame-work composition and cations associated with different stability; hydrophilicity/hydrophobicity and acid-based properties
- ✓ A large amount of structures that can be chosen as shape-selective catalysts for different reactions.

1.4.1.2 Structure of Zeolites

The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Adjacent tetrahedra is linked at their corners via a common oxygen atom, and this results in an inorganic macromolecule with a structurally distinct three-dimensional framework. It is evident from this building principle that the net formulae of the tetrahedra are SiO_2 and AlO_2^- , i.e. one negative charge resides at each tetrahedron in the framework which has aluminum in its center (Ali *et al.,* 2003). The framework of a zeolite contains channels, channel intersections and/or cages with dimensions from ca. 0.2 to 1 nm. So, aluminosilicates have negatively charged oxide frameworks (one charge per framework Al^{3+}) which require charge-balancing by cations. Typical cations include the alkaline (Li^+, Na^+, K^+) and the alkaline earth (Mg^{2+}, Ca^{2+}, Ba^{2+}) ions, quaternary ammonium ions, protons (in the acid form of zeolites), and the rare earth and noble metal ions. The cations are quite mobile and may be exchanged by other cations, which determine the ion-exchange properties of the zeolites (Nowinska *et al.*, 2003).

Zeolites are crystalline networks of alumino-silicate, where the structural formula of zeolites is best expressed for the crystallographic unit cell as (Hashimoto, 2003):

$$M_{x/n}[\,(AlO_2^-)_x\,(SiO_2)_y].\,wH_2O \qquad (1.20)$$

Where M is the cation of valence n, the portion with [ ] represents the framework composition. The sum (x + y) is the total number of tetrahedral in the unit cell. The ratio x/y must be smaller than or equal to 1, since AlO_2^- tetrahedral can only join to SiO_2 tetrahedra according to the Lowenstein rule. w is the number of water molecules per unit cell. The water in many zeolites can be reversibly removed by calcinations, leaving an open host structure.

Structurally, zeolites are built of primary and secondary building units. The primary unit is simply the SiO_4 or AlO_4 tetrahedron. Si or Al atom sits at the center of the tetrahedron with 4 oxygen atoms co-valently bonded to the centered Si or Al atom (so-called T-atom). From this primary unit, a number of secondary building units can be built by a linkage through the oxygen atom covalent bonding, which is called an oxygen bridge (Weitkamp, 2000).The secondary building units are featured by simple geometric shapes such as those shown in Figure 1.9. A zeolite structure is finally constructed from the secondary units. A pore channel system is formed during the systematic packing of the secondary units (Ribeiro *et al.*, 1995). A schematic representation of the structuring process of a zeolite is shown in Figure 1.9.

Furthermore, zeolites were traditionally used as highly selective adsorbents, ion exchangers and catalysts with high activity and selectivity in a wide range of reactions. The unique properties of zeolites arise from their uniformity in pore size and the chemical composition. The pore size of zeolites was determined by the number of T atoms in the ring openings, where T is Si^{4+} or Al^{3+}. Zeolites with pores comprising of 8, 10, and 12 T atoms have historically been classified as small (8-member ring), medium (10-member ring), and large-pore zeolites (12-member ring) respectively (Weitkamp, 2000).These pores may extend in one-dimensional tunnels, two-dimensional intersecting cages and, finally, three-dimensional connected channel system of nanometer scale networks. This microporous pore system renders zeolites high surface area and allows zeolites to recognize, discriminate, and organize molecules with precisions that can be less than 1 Å (Roldan *et al.*, 2005). The molecular shape selectivity of zeolites results from the interaction of adsorbed molecules with zeolite channels or cages of atomic size. In addition, the characteristics of some typical zeolites are listed in Table 1.2.

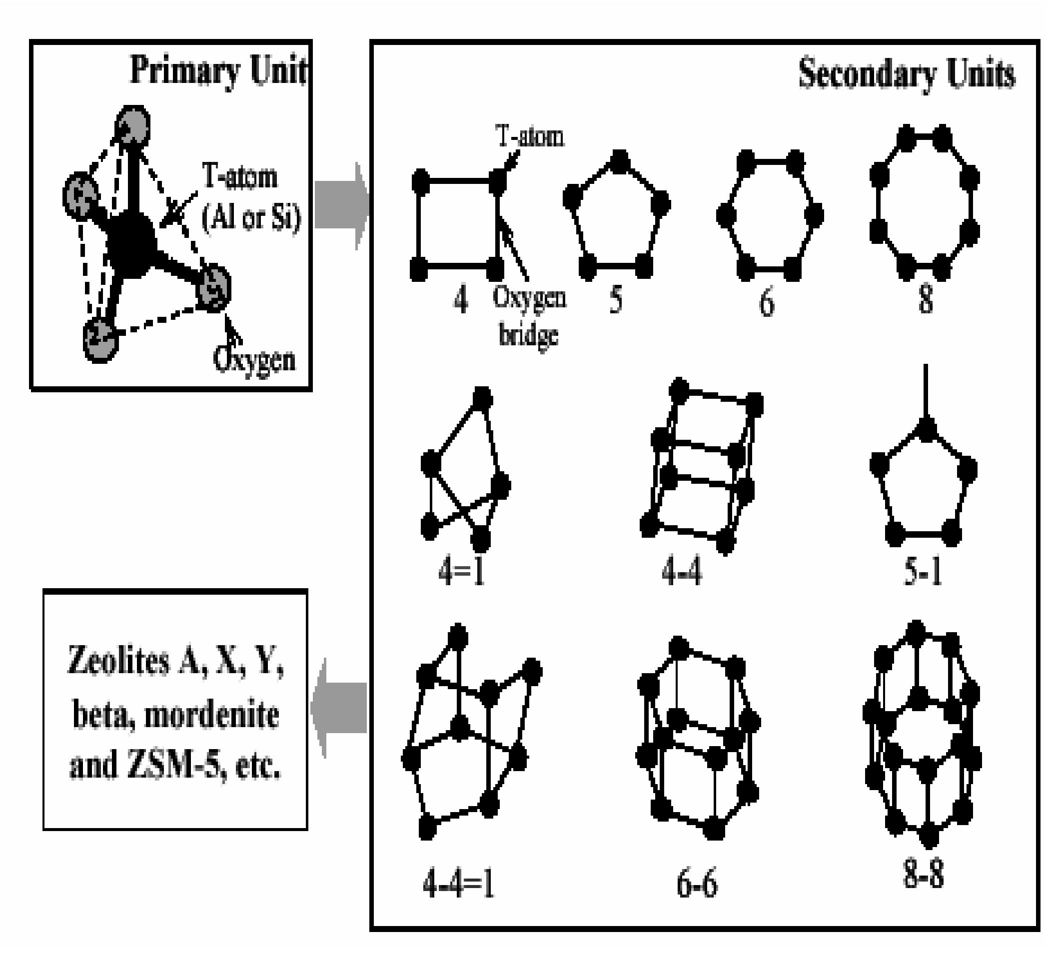

Figure 1.9 Schematic representation of building zeolites (Rabo, 1976)

Table 1.2: Characteristics of some typical zeolite porous material (Weitkamp, 1998)

Zeolite	Number of rings	Pore size (A)	Pore/Channel Structure
8-membered oxygen ring			
Erionite	8	3.6 x 5.1	Intersecting
10-membered oxygen ring			
ZSM-5	10	5.1 x 5.5	Intersecting
		5.3 x 5.6	
ZSM-11	10	5.3 x 5.4	Intersecting
Dual pore system			
Ferrierite	10,8	4.2 x 5.4	One dimensional
		3.5 x 4.8	10: 8 intersecting
Mordenite	12	6.5 x 7.0	One dimensional
	8	2.6 x 5.7	12: 8 intersecting
12-membered oxygen ring			
ZSM-12	12	5.5 x 5.9	One dimensional
Faujasite	12	7.4	Intersecting
		7.4 x 6.5	12: 12 intersecting
Mesoporous system			
VPI-5	18	12.1	One dimensional
MCM41-S	-	16-100	One dimensional

1.4.1.3 Mechanisms of the Shape Selectivity

In particular, zeolites usually show specific selectivity in some reactions due to their microporous properties. Because the pores of the zeolites are similar to many organic molecules of practical interest, it became possible to design novel catalysts which control the progress of the reactants and products through them via selecting the molecules by their size and shape, so called shape selective catalysts (Ramaswamy, 2003). It is generally believed that the majority of the active sites is located in the pores of zeolite (Corma, 2003).

Typically, five fundamental steps are involved in an overall reaction using zeolite as a catalyst : (i) diffusion of molecules from gas phase into the pores of the zeolites; (ii) adsorption of molecules on active sites; (iii) conversion of reactants molecules into product molecules; (iv) desorption of product molecules from active sites and eventually; (v) diffusion of product molecules into gas phase from the pores of the zeolite. The shape selectivity of the zeolite for a specific reaction may be possibly involved in step (i), (iii) or / and (v) (Krishna and Baur, 2003).

Based on different controlling steps, the shape selectivity of zeolites usually observed can be classified into three different types, including reactant shape selectivity, product shape selectivity and transition state selectivity, which are described in Figure 1.10.

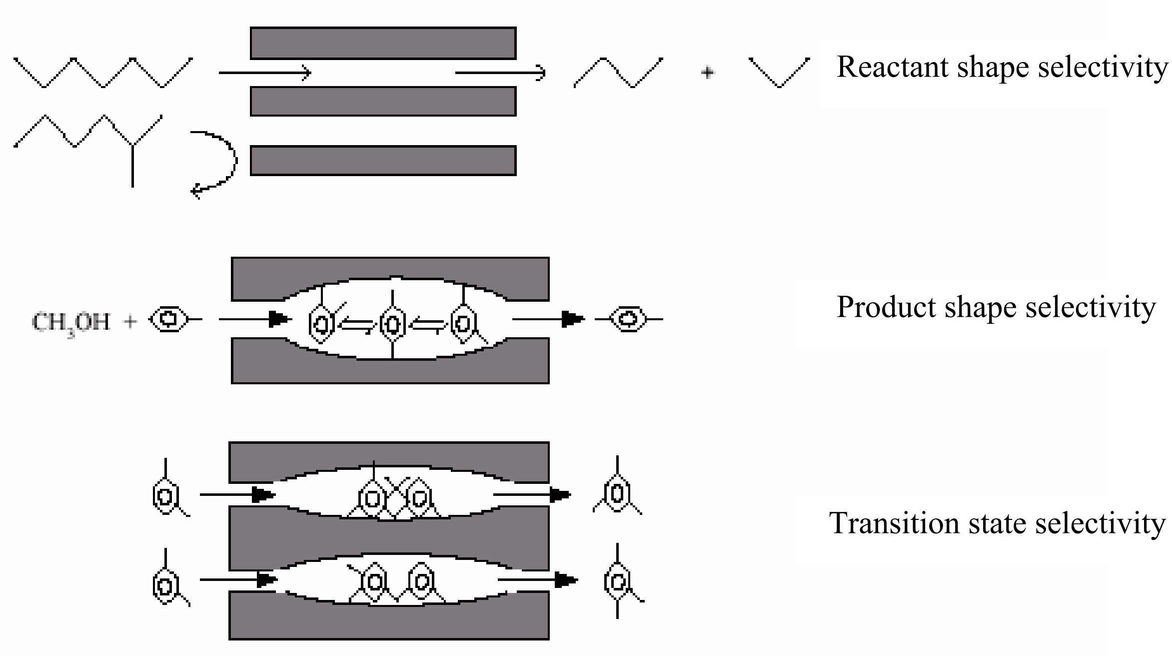

Figure 1.10 Schematic diagram of shape selectivity of zeolite (Krishna and Baur, 2003).

Reactant shape selectivity can be observed in the case of different participating reactant molecules with smaller and bulkier diameters compared to the pore entrance of zeolite. Reactants with smaller kinetic diameters can penetrate into the interior pores of zeolite and access the active sites located in the pores of the zeolite. Reactants with larger diameter, however, cannot diffuse into the pores of zeolite and the reaction with bulky reactant molecules involved can be encumbered.

Product shape selectivity occurs when some of the reaction products cannot escape from the zeolite due to their size or shape. Then these molecules can undergo a secondary reaction to form molecules that are able to leave the catalyst. Transition state selectivity is observed when both the reactant and product molecules fit well within the pores of the zeolite, while the reaction intermediates are larger than them and are spatially constrained either by their size or by orientation.

1.4.1.4 ZSM-5 Zeolite Catalyst

The type of zeolite catalyst used in this project is called Mobil Synthetic Zeolite-5 (ZSM-5), which was developed by Argauer and Landolt in 1972 (Gayubo *et al.*, 2003). Since its inception, ZSM-5 has been widely used for hydrocarbon inter conversion in the petroleum industry. ZSM-5 zeolites in protonic type (H-ZSM-5) have been extensively used in acid catalyzed reactions. H-ZSM-5 zeolites can be synthesized with a broad range of Si-Al ratio from 6 to infinity. In principle, the acid strength and acid types are the key properties of zeolites, which play a crucible role in the activity and selectivity of the zeolites. The range of zeolite-catalyzed reactions can be extended by the incorporation of metal atoms both inside and outside the zeolite framework (Goursot, *et al.* 2003).

The topology of the zeolite framework is given by a unique three-letter code, which is not related to the composition of the material. Generally, based on the pore openings, zeolites are referred to as small (8-member ring), medium (10-member ring) and large (12- member ring) pore zeolites. Thus, ZSM-5 is a medium pore zeolite materials with Mobil Five (MFI) topology (Rabo, 1976). The MFI structure is built up by 5-1 secondary building units (SBU; the smallest number of TO_4 units, where T is Si or Al, from which zeolite topology is built) which are linked together to form a chain (Figure 1.11) and the interconnection of these chains leads to the formation of the channel system in the structure (Klinowski and Barrie, 1988). The MFI structure has a three-dimensional pore system consisting of sinusoidal 10-ring channels (5.1 x 5.5 Å) and intersecting straight 10-ring channels (5.3 x 5.6 Å) and these two different channels are perpendicular to each other and generate intersections with diameters of 8.9 Å (Hashimoto, 2003).

For the Methanol to Gasoline (MTG) process, it is the pores created by these 10-oxygen rings, along with the zig-zag pores intersecting them that are essential to the formation of products that are desirable components of gasoline (Grobet, 1988). An 8-oxygen ring zeolite will not produce molecules with 6 or more carbons as molecules of this size will not fit into the small pores of these zeolites. The large pores of a 12-oxygen ring zeolite produce large amounts of C-11 and C-12 compounds, which are undesirable products for gasoline range hydrocarbons (Rabo, 1976).

On the other hand, most of ZSM-5 catalysts are used in oil refining and gas-conversion processes, such as the conversion and upgrading of the various fractions into transportation fuels, methanol-to-gasoline, conversion of syngas, light paraffins and olefins into gasoline and gasoil (Kerby *et al.*, 2005). A huge interest in ZSM-5 is due to its unique properties that have provided them a vast niche in the industry :

- ✓ High thermal and hydrothermal stability in the industrial environment, especially highly siliceous zeolites
- ✓ High internal surface area
- ✓ Presence of ion exchange ability allows the formation of highly dispersed catalytically active sites, such as highly acidic sites
- ✓ Pores structure provides shape selectivity (which has been shown to limit chain length growth to gasoline range hydrocarbons in methane conversion)
- ✓ High acidity promotes the oligomerisation, isomerisation, cracking and aromatisation reactions

The ZSM-5 type zeolite, which has all these properties, is the catalyst for this work due to its importance in the oligomerization processes.

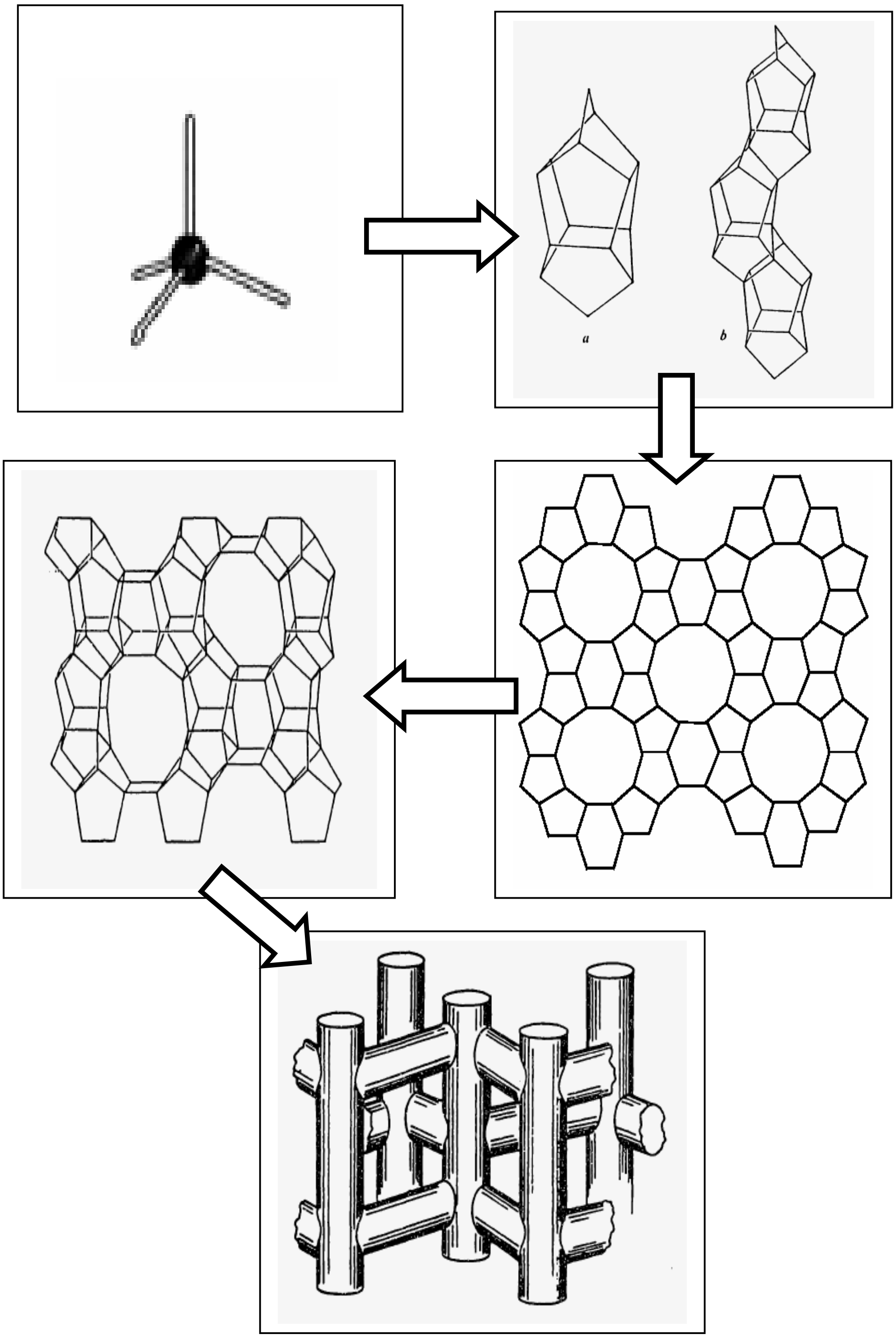

Figure 1.11 Illustration of primary unit of TO_4 tetrahedral, 5-1 secondary building units, the MFI framework and channel structure of ZSM-5 zeolite (Klinowski and Barrie, 1988)

1.4.2 Magnesium Oxide-based Catalysts for OCM Reactions

Metal oxides act as important catalysts in the reaction of oxidative coupling of methane (OCM). The catalytic reaction of OCM over metal oxide surfaces has been intensively investigated over the past 20 years (Lintuluoto and Nakamura, 2004). There are still ongoing studies to find good catalysts to achieve more active and especially higher selectivity toward C_2 hydrocarbon (especially ethylene). Among the solids used in OCM as the main components or supports of numerous active and selective oxide catalysts, magnesium oxide occupies a special position. Catalysts based on MgO promoted with alkali oxides, alkaline earth oxides, rare earth oxides, etc., have been frequently used in the research.

It is widely accepted that the increase in surface basicity caused by a promoter enhances the activity and C_2 selectivity (the selectivity to C_2H_4 and C_2H_6) of MgO-based catalysts (Maitra, 1993). Only limited attention had been given to the activity of unpromoted MgO itself in the OCM process and to the role of MgO as a carrier in MgO-based catalysts. As noticed by some authors, the samples of MgO differing in origin and properties usually also varied in their catalytic performance. This phenomenon was usually related to the differences in morphology, the specific surface area, surface structure and properties, a type of precursor, the calcination time and temperature, etc. (Burrows *et al.*, 1998; Lacombe *et al.*, 1995; Kus *et al.,* 2003; Kus *et al.*, 2002b, Kus and Taniewski, 2002; and Maksimov *et al.*, 1998).

Burrows *et al.* (1998) have pursued the structure sensitivity aspect of OCM catalyst design for MgO and doped MgO catalysts for a number of years. A perfect structure of MgO as a cubic (rocksalt) crystal is illustrated in Figure 1.12. However, under certain conditions or situations (such as addition of lithium), magnesium oxide has a highly defective surface structure showing steps, kinks, corners, and others which provide O^{2-} sites of low coordination. These low co-ordinated O^{2-} sites (O^{2-} on faces, O^{2-} on edges and O^{2-} on corners) are expected to be responsible for the strength of the basic sites (Pinarello, *et al.,* 2001).

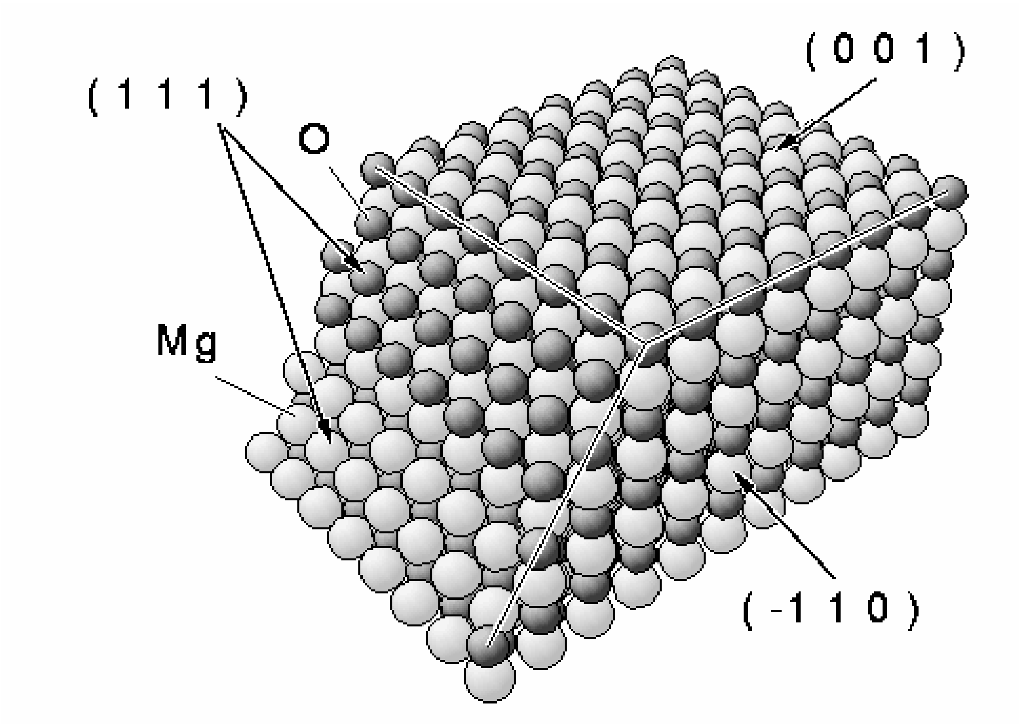

Figure 1.12 Cubic (rocksalt) MgO crystal: different planes (Hermann, 2002)

By comparing the microstructure and performance of pure MgO catalysts prepared by a number of very different routes, Burrows *et al.* (1998) have demonstrated that the selectivity and specific catalytic activity are unaffected by the number of corner or edge sites that the MgO exposes. That suggested that vacancies on the planar {100}-type surfaces of MgO are likely to be active sites for methane activation. They have also shown that the addition of lithium carbonate to MgO results in subtle changes in the surface structure. The improved catalytic performance of Li doped MgO was associated with, amongst other effects, the presence of dislocations creating active sites on the MgO surface.

The MgO properties/performance relationship still remains a controversial question. Although intensive investigations have been carried out, the nature of active sites formed in these oxides at high temperature are still a matter of debate. However, it is clear that the lattice defects of doped oxides play an important role in the reaction mechanism (Balint and Aika, 2001). This is not surprising since the lattice defects of a large number of oxide systems have been reported to play an important role in molecular activation at high temperatures. A part of the surface oxygen becomes active at high temperatures, reacting with methane even on irreducible oxides such as MgO. The special oxygen structure such as O^-, has been proposed as the active species. If O^- is the active species, O^- or the surface structure accepting O^- must be generated only at high temperature on MgO catalytic systems. Thus, it can be seen that the OCM reaction occurs on MgO only at high temperatures, usually 873–1073 K. Accordingly, Karasuda and Aika (1997) concluded that the OCM reaction occurs through such an activation step as is shown in Figure 1.13 when applying MgO based catalyst.

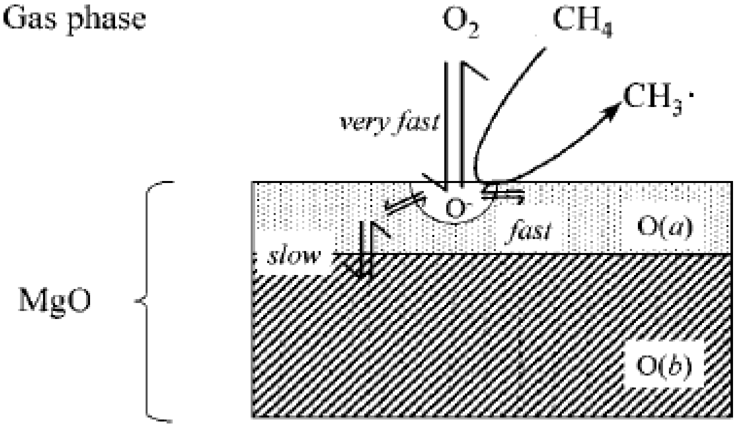

Figure 1.13 Model of oxygen atom flux in MgO-based catalysts where the fast exchange with an *a*-group O (O_a) in the MgO surface and the slow exchange with a b-group O (O_b) in MgO lattice (Karasuda and Aika, 1997)

Karasuda and Aika (1997) also focused their attention on MgO as a representative irreducible oxide for the OCM catalyst and have attempted to clarify the production mechanism of the active site. The authors have reported that the conductivity of MgO and Li/MgO is related to the defect structure produced by the decomposed impurity H_2O dissolved in the MgO lattice. The electric conduction is considered due to proton jumping at low temperatures, while hole conductivity prevails at high temperatures, where H_2O is dissolved in MgO (step 1 in Figure 1.14) and the hole ($O^{2-} + h^{+} = O^{-}$) is produced through H_2 evolution (step 2 in Figure 1.14). During the OCM reaction, O^{-} (or hole + O^{2-}) reacts with methane to produce methyl radical and OH^{-} (step 3 in Figure 1.14). Two methyl radicals combine to form ethane (and then ethene). The produced OH^{-} is removed as H_2O leaving the defect (step 4 in Figure 1.14) and dioxygen reproduces O^{-} again (step 5 in Figure 1.14). If methane is not present but dioxygen is at the OCM temperature (step 5 in Figure 1.14), then the reverse reaction (step 6 in Figure 1.14) can be observed through the isotopic exchange. Thus, the isotopic exchange between dioxygen and MgO provides significant information on the active center of the OCM reaction.

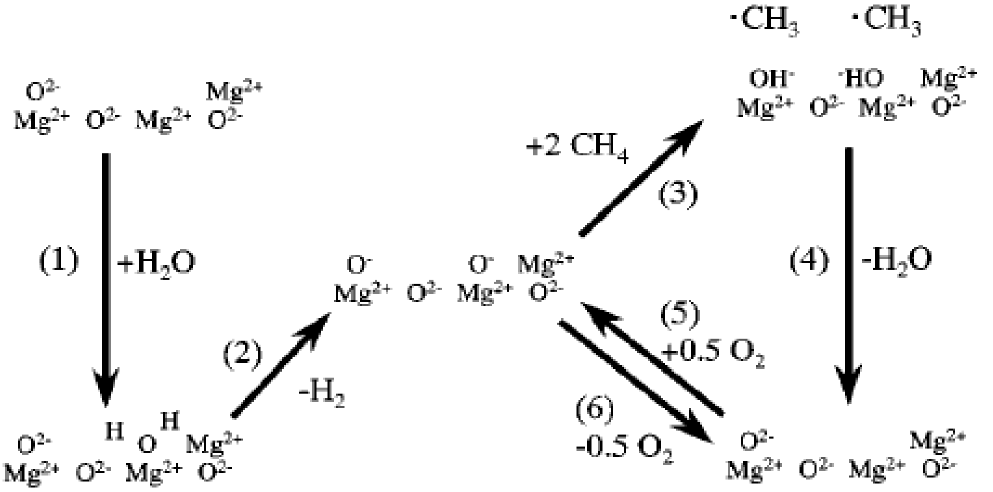

Figure 1.14 Model of active center generation and the OCM reaction model (Karasuda and Aika, 1997)

Currently, rare-earth-metal (REM) oxides, like La_2O_3, are among the most active catalysts for OCM, and a number of experimental studies centered around the mechanistic features of their chemistry have been reported. In the same way, Choudhary *et al.* (2000b) and Traykova *et al.* (1998) suggested that La-promoted MgO catalysts showed high activity and selectivity in the OCM process at a very high space velocity and also high catalyst stability in the process. The promotion effect of lanthanum was attributed to a large increase in the strong basicity of the catalyst because of the doping of MgO by lanthanum. Lacombe *et al.*, (1994) suggested that surface intermediates such as methoxide ions M-O-CH_3 are formed on the lanthanum oxide catalysts in the course of the OCM reaction. The formation of these species would be related to the dehydroxylation of terminal La-OH groups leading to the formation of a complex site {O^{2-}, vacancy}; this site would allow the adsorption of a methyl radical colliding with the surface. Once stabilized, the La-O-CH_3 species would undergo a further oxidation. Thus, specific hydroxyl groups from the lanthana surface could act as methyl radical scavengers. Because of its high activity/selectivity and productivity (i.e. operation at high space velocity or low contact time), and also high thermal stability, the La-promoted MgO catalyst has a high potential for use in the OCM process.

1.4 The Statement of Problem

Efficient utilization of methane, the primary component of natural gas, is becoming an immediate goal as we face issues of diminishing natural resources. Unfortunately, the remote locations of most natural gas reserves make transportation of this fuel economically unreasonable. One means to exploit the remote gas sources is to first convert methane to more useful higher carbon products that can easily be transported to the consuming facility. However, existing methane conversion methods have proven to be prohibitively expensive. Thus, developing a less expensive catalytic conversion method is of great interest and technologically significant.

In particular, the direct catalytic conversion of methane into desired chemicals or liquid fuels is still a great challenge for the utilization of natural gas in the field of catalysis. The two approaches involved are direct conversion of methane with the assistance of oxidants and direct conversion of methane under nonoxidative conditions. For example, the heterogeneously catalyzed oxidative coupling of methane (OCM) seems to be one of the most promising routes to convert methane directly from the abundant natural gas into ethylene which is a feed-stock for chemical industry and/or by oligomerization of ethylene into transportation fuels. A wide variety of catalysts, mainly metal oxide based catalysts, have been studied and reaction mechanisms have been proposed. Although significant progress has been achieved in the research and development of oxidative coupling of methane (OCM), it is still difficult to overcome the barriers of technical and economic problems. Two factors handicap commercialization of this process: (1) C_{2+} selectivity and yield are too low and (2) technological novelty results in uncertainty for scale-up. Higher C_{2+} selectivities and yields have to be achieved mainly by development of more selective catalysts, but optimization of reaction conditions, reactor design and operation also offers possibilities to improve catalytic performance.

The technological uncertainty is due to the fact that all results available until now have been achieved in laboratory-scale units, mainly in microcatalytic fixed-bed and small-scale fluidized-bed reactors. Due to the complexity of the OCM reaction scale-up can be associated with a loss in catalytic performance. Moreover, the severe reaction conditions, i.e. high temperature and exothermicity require new reactor designs. Therefore, experience from other selective oxidation reactions can be used only to a limited extent. Reactor development includes not only the choice of the reactor type but also the selection of materials and of the method of temperature control. Against this background, reaction engineering aspects of the OCM reaction play an important and crucial part in the attempt to make this process commercially viable.

In addition, one of the serious limitations of the OCM process is the low concentration of ethylene in the product stream. Separation of ethylene at a low concentration is not at all economical. One way to overcome this limitation of the OCM process is to convert the dilute ethylene present in the OCM product streams directly into much less volatile product streams, such as aromatics and/or gasoline range hydrocarbons, which can be easily separated. On the other hand, although OCM results in the production of hydrocarbons, this product is characterized by the lack of selectivity for a particular hydrocarbon type or carbon chain length. Hence, there is a great need for a highly active and selective ethylene transformation catalyst useful for converting ethylene at very low concentrations or partial pressures into liquid hydrocarbons. Consequently, a second catalyst becomes essential if selectivity for a particular product is required.

During the early days, H-ZSM-5 zeolite, which is one of the synthetic zeolite, was found to be a suitable catalyst for the conversion of methane to higher hydrocarbons. Later, ZSM-5 was modified to increase the conversion of methane and the selectivity of targeted hydrocarbons products. But, this catalytic process has not reached the commercializing stage and it needs development to obtain a more promising result. However, some earlier studies have demonstrated that acidic H-ZSM-5 zeolite catalyst has shown a reasonably good oligomerization performance for olefin products to higher hydrocarbons.

Taking advantages of both the exclusive functionality of OCM catalyst and good oligomerization activity of H-ZSM-5 catalyst, we propose here the dual catalyst bed concept. In the present study, we have applied these catalysts to a serial dual-bed system as an alternative methane conversion route to liquid hydrocarbons in the presence of oxygen. The development of a combination of an OCM catalysts and H-ZSM-5 would overcome the inherent limitations and permit the direct conversion of methane to liquid hydrocarbons via a single reactor process. Therefore, a reactor system with such a function would be the focus of in this research.

1.5 Hypothesis

Taking advantages of both the exclusive functionality of OCM catalyst and good oligomerization activity of H-ZSM-5 catalyst, we propose here the dual catalyst bed concept. In the present study, we have applied these catalysts to a serial dual-bed system as an alternative methane conversion route to liquid hydrocarbons in the presence of oxygen. The development of a combination of an OCM catalysts and H-ZSM-5 would overcome the inherent limitations and permit the direct conversion of methane to liquid hydrocarbons in order to solve the mystery of directly converting methane to liquid hydrocarbons via a single step reactor process. Therefore, a reactor system with such a function would be the focus of in this research.

The first catalyst comprises rare earth and alkaline earth metal oxides that are good materials for producing good-performance OCM catalysts and methane conversion. Rare earth oxides have been thought to be good catalysts for the OCM reaction, and alkaline earth oxides have been found to be good promoting materials for rare earth oxides. Therefore, the first catalyst is preferably lanthanum promoted MgO catalyst that is believed to give better C_2 selectivity. The second catalyst comprises an intermediate pore size zeolite, HZSM-5 which further provides shape selectivity (which has been shown to limit chain length growth to gasoline range hydrocarbons) and its high acidity is effective to promote the oligomerization, isomerization and aromatization reactions involved in the restructuring of the primary OCM products. Apart from that, recent research showed that that metal loaded HZSM-5 catalysts are suggested to be potential catalysts for direct conversion of methane to liquid hydrocarbons. Therefore, metal-containing HZSM-5 catalysts can produce C_{5+} liquids from OCM intermediate products if dehydrogenation and oligomerization functions of the metal are in balance. Hence, performance of the HZSM-5 catalysts with combination metals of (Ni, Mo and Cu) is tested through this research.

Furthermore, the process of this study is directed to converting high percentages of the methane present in mixed methane-oxygen containing feeds to OCM products at the first stage, while simultaneously converting mainly olefins to gasoline range liquid hydrocarbons at the second stage. In this way, the complexity of the separation processes needed in the ethylene recovery process also could be minimized.

1.6 Research Objectives

The main objectives of this research are:

i) To develop a lab scale dual-bed catalytic reactor system that is capable of catalyzing the production of liquid hydrocarbons from methane
ii) To elucidate the effect of reaction parameter on the dual- bed system

iii) To modify H-ZSM-5 with different kinds of metal and investigate the performance of this modified H-ZSM-5 catalysts on the products distribution as a function of types of metal.
iv) To find the optimum operating conditions required for maximum catalyst activity

1.7 Scope and Structure of this Thesis

This thesis focuses on the experimental study of a dual bed catalytic system over La-MgO and H-ZSM-5 based catalysts in accordance with the purposes of the present invention as embodied and broadly described herein, to produce liquid hydrocarbons from the methane gases. Thus, in this work, the possibility of liquid hydrocarbon production by means of the dual-bed system was investigated, and the effects of some reaction conditions were also explored. The focus is also given on the modification of the second bed catalyst of H-ZSM-5 by introducing some metal via incipient impregnation method in order to improve the yield of targeted products. Furthermore, it also involved the characterization of some catalysts in order to determine catalyst behavior. In addition, we report for the sequential optimization strategy for liquid hydrocarbons production through statistically designed experiments as an effective tool for medium engineering.

The thesis is divided into six chapters. Basically, an introduction with a short overview of the literature data on the particular topic is given in each chapter. In Chapter 1 the literature review which is related to the subject of this thesis has been reviewed briefly. The background regarding the properties of the zeolites and OCM catalysts are included in Chapter 1 as well as some theory on aspects of this research. The relevance of heterogeneous catalysis and the necessity to understand catalytic processes on microscopic scale are also accentuated. Furthermore, the fundamental concepts of catalytic conversion of methane is offered in this chapter. In addition, the applicability of our experimental approach to solve problems in applied catalysis is discussed. The objective of the research has also been elaborated in this section.

Chapter 2 outlines the experimental apparatus used and the experimental procedures. This chapter provides a brief description of the catalyst preparation procedures using conventional impregnation method. Moreover, the additional sections of this chapter focus on the general experimental procedures used throughout this work and the analytical techniques employed to interpret catalytic activity of all the catalysts. This chapter also describes the basic concept and the detailed procedures of the characterization method employed in this study.

Chapter 3 deals with the structural characterization and study the influence of the acidic behavior of the H-ZSM-5 catalyst in explaining the catalytic reaction performance of the dual bed system. Moreover, the influence of temperature and the effect of oxygen concentration on the activity and products selectivity as well as the result of the use of different SiO_2/Al_2O_3 ratio zeolite matrix were studied. A systematic approach is undertaken to study the influence of SiO_2/Al_2O_3 ratio and thermal treatment on the acidity and its nature, and the implication thereof for the intermediate OCM products conversion. The catalysts are characterized by TPD-ammonia techniques and the observed differences are correlated with the structural properties of the respective materials and catalytic activity.

Chapter 4 deals with the same system as Chapter 3 but focuses mainly on the role of metallic sites in order to obtain relations between the structural properties and the catalytic activity of the modified H-ZSM-5 catalysts in the conversion of methane through the dual bed strategy. The experimental phase was carried out in a dual-bed reactor in order to screen the catalysts and to identify the best one among the eleven metal-based H-ZSM-5 catalysts. The screening tests were conducted at fixed temperature of 700^0C and CH_4/O_2 ratio of 10. In this chapter, some of the important matter are addressed in explaining the advanced performance of metal based H-ZSM-5 catalysts in this dual bed system, compared with unloaded H-ZSM-5 when applied as second bed catalysts, under fixed other reaction parameters. Moreover, the simplified reaction scheme to describe the reaction path in this dual bed system proposed by employing the recent products spectra in light of the previous literature is also reported.

Chapter 5 describes a study to develop an approach that would enable us to better understand the relationships between the variables (temperature, oxygen concentration and amount of Ni loading (wt%) and the response (yield of C_{5+} hydrocarbons); and to obtain the optimum conditions for liquid hydrocarbons production using central composite design (CCD) and response surface methodology (RSM). The CCD has the advantage to predict responses based on a few sets of experimental data in which all factors are varied within a chosen range. The range of each variables was chosen based on the finding from one-factor at a time techniques. An empirical model including the effects of independent variables has also been developed through utilized software to represent the response surface. Also, TPD ammonia and NA characterization analysis were performed on the Ni loaded H-ZSM-5 catalysts to explicate the effect of modification of Ni on the catalytic reaction through the proposed system.

Finally, the results and findings of this thesis are summarized in Chapter 6. The future work possibilities are also suggested in this chapter.

REFERENCE

Abashar, M.E.E. (2004). Coupling of Steam and Dry Reforming of Methane in Catalytic Fluidized Bed Membrane Reactors. *International Journal of Hydrogen Energy*. 29: 799-808.

Aguiar, E. F. S, Appel, L.G. and Mota, C. (2005). Natural Gas Chemical Transformations: The Path to Refining in the Future. *Catalysis Today.* 101: 3-7.

Air Liquide Ltd. (2002). *Material Safety Data Sheet*.

Akhmedov, V.M., Soliman, H., Al-Khowaiter and Al-Refai, J.K. (2003). Hydroconversion of C_5-C_8 Alkanes over Zr-containing Supported Catalysts Prepared by Metal Vapor Method. *Applied Catalysis A: General.* 252: 353-361.

Aktas, N. (2005).Optimization of Biopolymerization rate By Rsponse Surface Methodology (RSM). *Enzyme and Microbial Technology.* (In Press).

Ali, M.A., Brisdon, B. and Thomas, W.J. (2003). Synthesis, Characterization and Catalytic Activity of ZSM-5 Zeolites Having Variable Silicon-to aluminum Ratios. *Applied Catalysis A: General*. 252: 149-162.

Alkhawaldeh, A., Wu, X., and Anthony, R.G. (2003). Conversion of Mixtures of Methane and Acetylene or Ethylene into Higher Molecular Weight Hydrocarbons over Metal-loaded and Unloaded HZSM-5 Zeolite Catalysts. *Catalysis Today*. 84: 43-49.

Amin, N.A.S and Anggoro, D.A. (2002). Dealuminated ZSM-5 Zeolite Catalyst for Ethylene Oligomerization to Liquid Fuels. *Journal of Natural Gas Chemistry.*11: 79-86.

Amin, N.A.S. and Anggoro, D.D. (2003). Characterization and Activity of Cr, Cu and Ga Modified ZSM-5 for Direct Conversion of Methane to Liquid Hydrocarbons. *Journal of Natural Gas Chemistry.* 12 : 123-134.

Amin, N.A.S. and Kusmiyati. (2004). Improved Perfomance of W/HZSM-5 Catalysts for Dehydroaromatization of Methane, *Journal of Natural Gas Chemistry*. 13: 148-159.

Andersson, J. and Redhe, M. (2003). *Response Surface Methods and Pareto Optimization in Crashworthiness Design.* Proceedings of DETC'03- ASME 2003 Design Engineering Technical Conferences and Computers and Information in Engineering Conference, Chicago, Illinois, USA.

Anshits, A.G., Kondratenko, E.V., Voskresenskaya, E.N., Kurteeva, L.I. and Pavlenko, N.I. (1998). The Influence of O_2 on Oxidative Coupling of Methane over Oxide Catalysts Using N_2O Oxidant. *Catalysis Today.* 46: 211-216.

Anunziata,O.A., Griselda A, Eimar and Pierella, L.B. (2000). Catalytic Conversion of Natural Gas with Added Ethane and LPG over Zn-ZSM-11. *Applied Catalysis A: General.* 190: 169-176.

Aoki, H. (2004). Design of Electron Correlation Effects in Interfaces and Nanostructures. *Applied Surface Science.* 237 : 2-12.

Araujo, L.R.R. and Schmal, M. (2002). Pt-Cr/ZSM-5 Catalysts for Propane and Cyclohexane Conversions. *Applied Catalysis A: General.*235: 139-147.

Arcoya A., Seoane X.L., and Grau J.M. (2003). Surface Characterization and Dehydrocyclization Activity of Pt/KL Catalysts Prepared by Different Methods. *Applied Surface Science.* 205: 206-211.

Arik, I.C., Denayer, J.F. and Baron, G.V. (2003). High-temperature Adsorption of n-alkanes on ZSM-5 Zeolites: Influence of the Si/Al Ratio and the Synthesis Method on the Low-coverage Adsorption Properties, *Microporous and Mesoporous Materials.* 60: 111-124.

Asadullah, M., Miyazawa,T., Ito, S., Kunimori, K., Yamada M. and Tomishige K. Catalyst Development for the Gasification of Biomass in the Dual-bed Gasifier. *Applied Catalysis A: General.* 255: 169-180.

Ashley, M. , Gamlin, T. and Freide, J.F. (2003). The Ultimate 'clean' Fuel-Gas-to-Liquid Products. *Hydrocarbon Processing*. February.

Ashman, P. J. and Mullinger, P. J. (2005). Research Issues in Combustion and Gasification of Lignite. *Fuel* 84: 1195-1205.

Baba, T. and Abe, Y. (2003). Metal Cation-acidic Proton Bifunctional Catalyst for Methane Activation: Conversion of $^{13}CH_4$ in the Presence of Ethylene over Metal Cations-loaded H-ZSM-5. *Applied Catalysis A: General* 250: 265-270.

Baerns, M. And Buyevskaya, O. (1998). Simple Chemical Processes Based on Low Molecular-mass Alkanes as Chemical Feedstock. *Catalysis Today*. 45: 13-22.

Balint, I. and Aika, K.I. (2001). Specific Defect Sites Creation by Doping MgO with Lithium and Titanium. *Applied Surface Science.* 173: 296-306.

Banares, M.A. (1999). Supported Metal Oxide and Other Catalysts for Ethane Conversion: A Review. *Catalysis Today.* 51: 319-348.

Barbero, J.A., Banares, M.A., Pena, M.A. and Fierro, J.L.G. (2001). Partial Oxidation of Methane into C_1-Oxygenates: Role of Homogeneous Reactions and Catalyst Surface Area. *Catalysis Today.* 71 :11-19.

Barr, T.L. (1990). The Nature of the Relative Bonding Chemistry in Zeolites: An XPS Study. *Zeolites. 10: 760-765.*

Barr, T.L. (1995). Comparative Electron Spectroscopy for Chemical Analysis and Nuclear Magnetic Resonance Analysis of High-surface Area Materials: Zeolites. *Microporous Materials.* 3 : 557-564.

Bartholomew, C.H. (2001). Mechanisms of Catalyst Deactivation. *Applied Catalysis A: General.* 212: 17-60.

Benyounis, K.Y., Olabi, A.G. and Hashmi, M.S.J. (2005). Optimizing the Laser-Welded Butt Joints of Medium Carbon Steel Using RSM. *Journal of Materials Processing Technology.* 164-165: 986-989.

Bhasin, M.M., McCain, J.H., Vora, B.V., Imai, T. and Pujado, P.R. (2001). Dehydrogenation and Oxydehydrogenation of Paraffins to Olefins. *Applied Catalysis A: General.* 221: 397-419.

Birol, F. and Argiri, M. (1999). World Energy Prospects to 2020. *Energy*. 24 : 905-918.

Biscardi, J.A. and Iglesia, E. (1996). Structure and Function of Metal Cations in Light Alkane Reactions Catalyzed by Modified H-ZSM-5. *Catalysis Today.* 31: 207-231.

Blaser, H.U. (2000). Heterogeneous Catalysis for Fine Chemicals Production. *Catalysis Today.* 60: 161-165.

Blowers, P. and Masel, R. (1998). Consevation of Bond Order During Hydrogenolysis and Dehydrogenation Reactions. *Surface Science.* 417: 238-246.

Bokhoven, J.A.V., Williams, B.A., Ji, W., Koningsberger, D.C., Kung, H.H. and Miller, J.T. (2004). Observation of a Compensation Relation for Monomolecular Alkane Cracking by Zeolites: the Dominant Role of Reactant Sorption. *Journal of Catalysis.* 214: 50-59.

Bond, G. C. (2000). Relativistic Effects in Coordination, Chemisorption and Catalysis. *Journal of Molecular Catalysis A: Chemical.* 156: 1-20.

Bond, G.C. and Hooper, A.D. (2000). Modification of Ruthenium Catalysts for Alkane Hydrogenolysis. *Applied Catalysis A: General.* 191: 69-81.

Bond, G.C. and Slaa, J.C. (1996). Catalytic and Structural Properties of Ruthenium Bimetallic Catalysts: Hydrogenolysis of Propane and n-Butane on Ru/Al_2O_3 Catalysts Modified by a Group 14 Element. *Journal of Molecular Catalysis. A: Chemical.* 106: 135-149.

Bond, G.C., Hooper, A.D., Slaa, J.C. and Taylor, A.O. (1996). Kinetics of Metal-Catalyzed Reactions of Alkanes and the Compensation Effect. *Journal of Catalysis*. 163: 319-327.

Borchert, H. and Baerns, M. (1997). The Effect of Oxygen- Anion Conductivity of Metal-Oxide Doped Lanthanum Oxide Catalysts on Hydrocarbon Selectivity in the Oxidative Coupling of Methane. *Journal of Catalysis*. 168: 315-320.

Borges, P., Pinto, P.R., Lemos, M., Lemos, F., Vedrine, J.C., Derouane, E.G. and Ribeiro, F.R. (2005). Activity-acidity Relationship for Alkane Cracking over Zeolites: n-hexane Cracking over HZSM-5. *Journal of Molecular Catalysis A: Chemical*. 229: 127-135.

Boudart, M. (1997). Heterogeneous Molecular Catalysis: Oxymoron or Reality? *Journal of Molecular Catalysis A: Chemical.* 120: 271-280.

Braunstein, P., Chauvin, Y., Mercier, S. and Saussine, L. (2005). Influence of Intramolecular N-H-O-Ni Hydrogen Bonding in Nickel(II) Diphenylphosphinolate Phenyl Complexes on the Catalytic Oligomerization of Ethylene. *C.R. Chimie.* (In Press).

Brunner, E., Beck, K., Koch, M., Heeribout, L. and Karge, H.G. (1995).Verification and Quantitative Determination of a New Type of Brønsted Acid sites in H-ZSM-5 by ^{1}H Magic-angle Spinning Nuclear Magnetic Resonance Spectroscopy. *Microporous Materials*. 3:395-399.

Buchanan, J.S. and Adewuji, Y.G. (1996). Effects of High Temperature and High ZSM-5 Additive Level on FCC Olefins Yields and Gasoline Composition. *Applied Catalysis A: General.* 134: 247-262.

Burrows, A., Kiely, C.J., Hargreaves, J.S.J., Joyner, R.W., Hutchings, G.J., Sinev, M.K. and Tulenin, Y.P. (1998). Structure/Function Relationships in MgO-Doped Nd_2O_3 Catalysts for the Methane Coupling Reaction. *Journal of Catalysis.* 173: 383-398.

Camiloti, A.M., Jahn, S.L., Velasco, N.D., Moura, L.F. and Cardoso, D. (1999). Acidity of Beta Zeolite Determined by TPD of Ammonia and Ethylbenzene Disproportionation. *Applied Catalysis A: General.* 182: 107-113.

Campbell, S.M., Bibby,D.M., Coddington, J.M., Howe, R.F. and Meinhold, R.H. (1996). Dealumination of HZSM-5 Zeolites I. Calcination and Hydrothermal Treatment. *Journal of Catalysis*. 161: 338-349.

Canizares, P., Lucas, A.D., Dorado, F. and Perez, D. (2000). Effect of Zeolite Pore Geometry on Isomerization of *n*-butane. *Applied Catalysis A: General.* 190: 233-239.

Carlini, C., Marchionna, M., Galletti, A.M. and Sbrana, G. (2001). Novel α-Nitroketonate Nickel(II) Complexes as Homogeneous Catalysts for Ethylene Oligomerization. *Applied Catalysis A: General*. 206: 1-12.

Casci, J. L. (2005). Zeolite Molecular Sieves: Preparation and Scale-up. *Microporous and Mesoporous Materials.* 82 (In Press).

Castellon, E.R., Lopez, A.J., Torres, P.M., Jones, D.J., Roziere, J., Trombetta, M., Busca, G., Lenarda, M. and Storaro, L. (2003). Textural and Structural Properties and Surface Acidity Characterization of Mesoporous Silica-zirconia Molecular Sieves. *Journal of Solid State Chemistry.* 175: 159-169.

Cavani, F. and Trifiro, F. (1995). The Oxidative Dehydrogenation of Ethane and Propane as an Alternative Way for the Production of Light Olefins. *Catalysis Today.* 24: 307-313.

Cavani, F. and Trifirò, F. (1999). Selective Oxidation of Light Alkanes: Interaction Between the Catalyst and the Gas Phase on Different Classes of Catalytic Materials. *Catalysis Today.* 51: 561-580.

Chang, Y.F., Somorjai, G.A. and Heinemann, H. (1995). An $^{18}O_2$ Temperature-Programmed Isotope Exchange Study of Transition-Metal-Containing ZSM-5 Zeolites Used for Oxydehydrogenation of Ethane. *Journal of Catalysis.* 154 : 24-32.

Chatterjee, A. and Vetrivel, R. (1996). Simulation Studies on the Role of Templating Organic Molecules in the Synthesis of Microporous Materials: 2. Modeling the Electronic Interaction Between the Templating Molecules and ZSM-5. *Journal of Molecular Catalysis A: Chemical.* 106 : 75-81.

Chen, B., Dingerdissen, U., Krauter, J.G.E., Lansink, H.G.J., Mobus, K., Ostgard, D.J., Panster, P., Riermeier, T.H., Seebald, S., Tacke, T. and Trauthwein, H. (2005a). New Developments in Hydrogenation Catalysis Particularly in

Synthesis of Fine and Intermediate Chemicals. *Applied Catalysis A: General* 280: 17-46.

Chen, F., Cai, T., Zhao, G., Liao, X., Guo, L.and Hu, X. (2005). Optimizing Conditions for the Purication of Crude Octacosanol Extract from Rice Bran Wax by Molecular Distillation Analyzed using response Surface Methodology. *Journal of Food Technology.* 70: 47-53.

Chen, L., Lin, L., Xu, Z., Li, X., and Zhang, T. (1995). Dehydro-Oligomerization of Methane to Ethylene and Aromatics over Molybdenum/HZSM-5 Catalyst. *Journal of Catalysis.* 157: 190-200.

Chen, M.J., Chen, K.N. and Lin, C.W. (2005b). Optimization on Response Surface Models for the Optimal Manufacturing Conditions of Dairy Tofu. *Journal of Food Engineering.* 68: 471-480.

Cheung, T.K. and Gates, B.C. (1997). Activation of Ethane in the Presence of Solid Acids: Sulfated Zirconia, Iron- and Manganese- Promoted Sulfated Zirconia, and Zeolites. *Journal of Catalysis.* 168. 522-531.

Chiang, W.D., Shih, C.J. and Chu, Y.H. (2001). Optimization of acid hydrolysis conditions for total isoflavones analysis in soybean hypocotyls by using RSM. *Food Chemistry.* 72: 499-503.

Cho, W., Lee, S.H., Ju, W.S., Baek, Y. and Lee, J.K. (2004). Conversion of Natural Gs to Hydrogen and Carbon Black by Plasma and Application of Plasma Carbon Black. C*atalysis Today*. 98: 633-638.

Choi, E.Y., Nam, I.S. and Kim, Y.G. (1996). TPD Study of Mordenite-Type Zeolites for Selective Catalytic Reduction of NO by NH_3. *Journal of Catalysis.* 161: 597- 604.

Chou, L., Cai, Y., Zhang, B., Niu, J., Ji, S. and Li, S. (2003). Influence of SnO_2-doped W-Mn/SiO_2 for Oxidative Conversion of Methane to High Hydrocarbons at Elevated Pressure. *Applied Catalysis A.* 238: 185-191.

Choudhary, V.R. and Mulla, S.A.R. (2001a). Energy Efficient Simultaneous Oxidative Conversion and Thermal Cracking of Ethane to Ethylene Using Supported BaO/La_2O_3 Catalyst in the Presence of Limited O_2. *Applied Energy*. 68: 377-386.

Choudhary, V.R., Mulla, S.A.R. and Rane, V.H. (2000a). Coupling of Exothermic and Endothermic Reactions in Oxidative Conversion of Ethane to Ethylene over Alkaline Earth Promoted La_2O_3 Catalysts in Presence of Limited O_2. *Applied Energy. 66*: 51-62.

Choudhary, V.R., Rane, V.H. and Chaudhari, T. (1997). Surface Properties of Rare Earth Promoted MgO Catalysts and Their Catalytic Activity/Selectivity in Oxidative Coupling of Methane, *Applied Catalysis A: General*. 58: 121-136.

Choudhary, V.R., Banerjee, S. and Panjala, D. (2002). Product Distribution in the Aromatization of Dilute Ethene over H-Ga-AlMFI Zeolite: effect of space velocity. *Microporous and Mesoporous Materials.* 51 : 203-210.

Choudhary, V.R., Devadas, P., Banerjee, S. and Kinage, A.K. (2001b). Aromatization of Dilute Ethylene Over Ga- Modified ZSM-5 Type Zeolite Catalysts. *Microporous and Mesoporous Materials.* 47 : 253-267.

Choudhary, V.R., Mulla, S.A.R. and Uphade, B.S. (1999a). Oxidative Coupling of Methane over Alkaline Earth Oxides Deposited on Commercial Support Precoated With Rare Earth Oxides. *Fuel.* 78: 427-437.

Choudhary, V.R., Rane, V.H. and Chaudhari, S.T. (2000). Factors Influencing Activity/Selectivity of La- and Mg- Acetates for Oxidative Coupling of Methana, *Fuel.* 79: 1487-1491.

Choudhary, V.R., Sivadinarayana , C., Kinage, A.K., Devadas, P. and Guisnet, M. (1995). H-Gallosilicate (MFI) propane Aromatization Catalyst Influence of Calcination Temperature on Acidity, Activity and Deactivation Due to Coking. *Applied Catalysis A: General.* 136:125-142.

Choudhary, V.R., Sivadinarayana, C., Kinage, A.K., Devadas, P. and Guisnet, M. H-Gallosilicate (MFI) Propane Aromatization Catalyst, Influence of Calcination Temperature on Acidity, Activity and Deactivation Due to Coking. (1996). *Applied Catalysis A: General.* 136: 125-142.

Chouhary, V.R., Mulla, S.A.R. Uphade, B.S. (1999b). Oxidative Coupling of Methane over Alkaline Earth Oxides Deposited on Commercial Support Precoated With Rare Earth Oxides. *Fuel.* 78: 427-437.

Cora, F., Alfredsson, M., Barker, C.M., Bell, R.G., Foster, M.D., Saadoune, I., Simperler, A. and Catlow, R.A. (2003). Modelling the Framework Stability and Catalytic Activity of Pure and Transition Metal-doped Zeotypes. *Journal of Solid State Chemistry.* 176. 496-529.

Corma, A. (1995). Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. *Chemical Reviews.* 95: 559-614.

Corma, A. (2003). State of the Art and Future Challenges of Zeolites as Catalysts. *Journal of Catalysis.* 216: 298-312.

Corma, A., Nieto, J.M.L. and Paredes, N. (1997). Oxidative Synthesis of Aromatics from Propane on Mixed VMgO-zeolite Catalytsts. *Journal of Molecular Catalysis A: Chemical.* 123: 75-84.

Costine, A., Sullivan, T.O. and Hodnett, B.K. (2005). Oxidative Competition Between Aliphatic and Aromatic C-H bonds in the N_2O-Fe-ZSM-5 System. *Catalysis Today.* 99: 199-208.

Creyghton, E. J., Elings, J. A., Downing, R. S., Sheldon, R. A. and Bekkum, H.V. (1996). New multifunctional probe for testing outer surface activity of zeolites: application to surface-located platinum clusters and acid sites. *Microporous Materials.* 5 :299-307.

Creyghton, E.J. and Downing, R.S. (1998). Shape-selective Hydrogenation and Hydrogen Transfer Reactions over Zeolite Catalysts. *Journal of Molecular Catalysis A: Chemical.* 134: 47-61.

Davydov, A.A., Shepotko, M.L. and Budneva, A.A. (1995). Basic Sites on the Oxide Surfaces: Their Effect on the Catalytic Methane Coupling. *Catalysis Today*. 24: 225-230.

Dehertog, W.J.H. and Fromen, G.F. (1999). A Catalytic Route for Aromatics Production from LPG. *Applied Catalysis A: General.* 189: 63-75.

Dong, W.S., Roh, H.S., Jun, K.W., Park, S.E. and Oh, Y.S. (2002). Methane Reforming over Ni/Ce-ZrO_2 Catalysts: Effect of Nickel Content. *Applied Catalysis A: General.* 226: 63-72.

Du, J., Li, L.J. and Li, Y. (2005). Ni(II) Complexes Bearing 2-Aryliminobenzimidazole: Synthesis, Structure and Ethylene Oligomerization Study. *Inorganic Chemistry Communications*. 8: 246-248.

Editorial. (2003). An overview to 'Advances in C1 Chemistry in the year 2002'. *Fuel Processing Technology*. 83 : 1-9.

Edwards, I.M. and Jutan, A. (1996). Optimization and Control Using Response Surface Methods. *Computers.* 21: 441-453.

Elmasides, C. and Verykios, X.E. (2001).Mechanistic Study of Partial Oxidation of Methane to Synthesis Gas over Modified Ru/TiO_2 Catalyst. *Journal of Catalysis.* 203: 477-486.

Erdem, E., Karapinar, N. and Donat, R. (2004). The Removal of Heavy Metal Cations by Natural Zeolites. *Journal of Colloid and Interface Science* 280: 309-314.

Erena, J., Arandes, J.M., Bilbao, J., Gayubo, A.G., and Lasa, H.I.D. (2000). Conversion of Syngas to Liquid Hydrocarbons Over A Two-Component (Cr_2O_3-ZnO and ZSM-5 Zeolite) Catalyst: Kinetic Modelling and Catalyst Deactivation, *Chemical Engineering Science.* 55: 1845-1855.

Ermakova, M.A., Ermakov, D.Y. and Kuvshinov, G.G. (2000).Effective Catalysts for Direct Cracking of Methane to Produce Hydrogen and Filamentous Carbon. *Applied Catalysis A: General.* 201: 61-70.

Espinoza, R. L., Korf, C. J., Nicolaides, C. P. and Snel, R. (1987a).Catalytic Oligomerization of Ethene over Nickel-exchanged Amorphous Silica-alumina; Effect of the Reaction Conditions and Modelling of the Reaction. *Applied Catalysis. 29: 175-18.*

Espinoza, R. L., Nicolaides, C. P., Korf, C. J. and Snel, R. (1987b).Catalytic Oligomerization of Ethene over Nickel-exchanged Amorphous Silica-alumina; Effect of the Nickel Concentration. *Applied Catalysis. 31: 259-266.*

Espinoza, R. L., Snel, R., Korf, C. J. and Nicolaides, C. P. (1987c). Catalytic Oligomerization of Ethene over Nickel-exchanged Amorphous Silica-aluminas; Effect of the Acid Strength of the Support. *Applied Catalysis. 29: 295-303.*

Espinoza, R.L., Steynberg, A.P., Jager,B. and Vosloo, A.C. (1999). Low Temperature Fischer-Tropsch Synthesis from a Sasol Perspective. *Applied Catalysis A: General.* 286 : 23-26.

Fang, K., Ren, J. and Sun, Y. (2005). Effect of Nickel Precursors on the Performance of Ni/AlMCM-41 Catalysts for *n*-dodecane Hydroconversion. *Journal of Molecular Catalysis A: Chemical.* 229: 51-58.

Fang, K., Wei, W., Ren, J. and Sun, Y. (2004). n-Dodecane Hydroconversion over Ni/AlMCM-41 Catalysts. *Catalysis Letter.* 93:3-4.

Feng, M.H. and Chao, K.J. (1996). Quantum calculations of Brønsted acidity and ^{1}H NMR chemical shift in zeolites. *Journal of Molecular Structure: THEOCHEM.* 364:51-5.

Fogler, H. S. (1999). *Elements of Chemical Reaction Engineering*. 3rd ed. New Jersey: Prentice Hall Inc.

Forni, L., Vatti, F.P. and Ortoleva, E. (1995). Temperature-programmed Desorption-Diffusion of Ammonia in Molecular Sieves V. ZSM-5 zeolite. *Microporous Materials.* 3: 367-375.

French, S.A., Sokol, A.A., To, J., Catlow, C.R.A., Phala, N.S., Klatt, G. and Catlow, C.R.A. (2004). Active Sites for Heterogeneous Catalysis by Functionalisation of Internal and External Surfaces. *Catalysis Today.* 93-95: 535-540.

García, C.L. and Resasco, D.E. (1987). Promoter Action of KCl on $CuCl_2/SiO_2$ Catalysts used for the Oxyhydrochlorination of Methane. *Applied Catalysis.* 29:55-66.

Gayubo, A. G., Aguayo, A. T., Olazar, M., Vivanco, R., Bilbao, J. (2003). Kinetics of the Irreversible Deactivation of the HZSM-5 Catalyst in the MTO Process. *Chemical Engineering Science.* 58: 5239-5249.

Gesser, H.D. and Hunter, N.R. (1998). A Review of C-1 Conversion Chemistry. *Catalysis Today*. 42: 183-189.

Gheit, A.K.A., Fotouh, S.M.A. and Gheit, N.A.K. (2005). Hydroconversion of Cylohexene Using Catalysts Containing Pt, Pd, Ir and Re Supported on H-ZSM-5 Zeolite. *Applied Catalysis A: General.* (In Press).

Gokowska, A.K., Piotrowska, A.M. and Rutkowski, J.D. (2004). Oxidation of chlorinated hydrocarbons over Pt–Pd-based catalyst: Part 1. Chlorinated methanes. *Catalysis Today.* 90: 133-138.

Goursot, A., Coq, B. and Fajula, F. (2003). Toward a Molecular Description of Heterogeneous Catalysis: Transition Metal Ions in Zeolites. *Journal of Catalysis*. 216: 324-332.

Gradassi, M.J. and Green, N.W. (1995). Economics of Natural Gas Conversion Processes. *Fuel Processing Technology.* 42: 65-83.

Grobet, P. J. (1988). *Innovation in Zeolite Materials Science*. Amsterdam : Elsevier.

Guha, S. and Francisco, J.S. (2001). An Ab Initio Study of the Hydrogen Abstraction Reaction of Methane by Bromide Atoms and Bromide Monoxide Radicals. *Journal of Molecular Structure (Theochem).* 573: 171-180.

Guisnet, M. and Gnep, N.S. (1996). Mechanism of Short-chain Alkane Transformation over Protonic Zeolites. Alkylation, Disproportionation and Aromatization. *Applied Catalysis A: General*: 146 : 33-64.

Guo, X., Shen, J., Sun, L., Song, C. and Wang, X. (2004). Effect of SiO_2/Al_2O_3, MgO Modification and Hydrothermal Treatment on the Catalytic Activity of HZSM-5 Zeolites in the Methylation of 4-methylbiphenyl with Methanol. *Applied Catalysis A: General.* 261: 183-189.

Guo, X.Y., Liu, Z.W. and Zhong, B. (1998). Monte Carlo Simulation of Coke Formation in Zeolites. *Microporous and Mesoporous Materials.* 23: 203-209.

Ha, V.T.T., Tiep,L.V., Meriaudeau, P. and Naccache, C. (2002). Aromatization of Methane over Zeolite Supported Molybdenum: Active Sites and Reaction Mechanism. *Journal of Molecular Catalysis A: Chemical.* 181: 283-290.

Haller, G. L. (2003). New Catalytic Concepts from New Materials: Understanding Catalysis from a Fundamental Perspective, Past, Present, and Future. *Journal of Catalysis*. 216: 12-22.

Han, S., Martenak, D.J., Palermo, R.E., Pearson, J.A and Walsh, D.E. (1994). Direct Partial Oxidation of Methane Over ZSM-5 Catalyst: Metals Effects on Higher Hydrocarbon Formation. *Journal of Catalysis.* 148, 134-137.

Hashimoto, S. (2003). Zeolite Photochemistry: Impact of Zeolites on Photochemistry and Feedback from Photochemistry to Zeolite Science. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* 4: 19-49.

Heck, J.X., Hertz, P.F., Ayub, M.A.Z. (2005). Extraction Optimization of Xylanases Obtained Solid-state Cultivation of *Bacillus Circulans* BL53. *Process Biochemistry.* 40: 2891-2895.

Heemsoth, J., Tegeler, E., Roessner, F. and Hagen, A. (2001). Generation of Active Sites for Ethane Aromatization in ZSM-5 Zeolites by a Solid-state Reaction of Zinc Metal with Bronsted Acid Sites of the Zeolite. *Microporous and Mesoporous Materials*. 46 : 185-190.

Heracleous, E. and Lemonidou, A.A. (2004). Homogeneous and Heterogeneous Pathways of Ethane Oxidative and Non-oxidative Dehydrogenation Studied by Temperature-programmed Reaction. *Applied Catalysis A: General.* 269: 123-135.

Heracleous,E., Lee, A.F., Wilson, K. and Lemonidou, A.A. (2005). Investigation of Ni-based Alumina-supported Catalysts for the Oxidative Dehydrogenation of Ethane to Ethylene: Structural Characterization and Reactivity Studies. *Journal of Catalysis.* 231; 159-171.

Hermann, K. (2002). Gallery of BALSAC Pictures, Theory Department, Fritz-Haber-Institute, Berlin.

Heveling, J., Nicolaides, C.P. and Scurrell, M.S. (1998). Catalysts and Conditions for the Highly Efficient, Selective and Stable Heterogeneous Oligomerization of Ethylene. *Applied Catalysis A: General.* 173: 1-9.

Heydenrych, M.D., Nicolaides, C.P. and Scurrell, M.S. (2001). Oligomerization of Ethene in a Slurry Reactor Using a Nickel(II)-exchanged Silica-alumina Catalyst. *Journal of Catalysis.* 197: 49-57.

Hollens, J.H., Dillons, C.J., Labinger, J.A. and Davis, M.E. (2003). A Substrate-versatile Catalyst for the Selective Oxidation of Light Alkanes. I. Reactivity. *Journal of Catalysis.* 218: 42-53.

Holzwarth, A., Denton, P., Zanthoff H. and Mirodatos, C. (2001). Combinatorial Approaches to Heterogeneous Catalysis: Strategies and Perspectives for Academic Research. *Catalysis Today.* 67: 309-318.

Hong, J.H. and Yoon, K.J. (2001). Oxidative Coupling of Methane over Calcium Chloride-promoted Calcium Chlorophosphate. *Applied Catalysis A: General.* 205: 253-262.

Hu, Y.H. and Ruckenstein, E. (1996). Transient Kinetic Studies of Partial Oxidation of CH_4. *Journal of Catalysis.* 158: 260-266.

Hulea, V. and Fajula, F. (2004). Ni-exchanged AlMCM-41-An efficient Bifunctional Catalyst for Ethylene Oligomerization. *Journal of Catalysis.* 225: 213-222.

Iglesia, E., Barton, D.G., Biscardi, J.A., Gines, M.J.L. and Soled, S.L. (1997). Bifunctional Pathways in Catalysis by Solid Acids and Bases. Catalysis Today. 38. 339-360.

Iglesia, E., Baumgartner, J.E. and Geoffrey L. (1992). Kinetic Coupling and Hydrogen Surface Fugacities in Heterogeneous Catalysis: I. Alkane

Reactions on Te/NaX, H-ZSM5 and Ga/H-ZSM-5. *Journal of Catalysis.* 134:549-571.

Isatadi and Amin, N.A.S. (2005). A Hybrid Numerical Approach Multi-responses Optimization of Process Parameters and Catalyst Composition in CO_2 OCM Process over CaO-MnO/CeO_2 Catalyst. *Chemical Engineering Journal.* 106: 213-227.

Ivanov, A.V., Graham, G.W. and Shelef, M. (1999). Adsorption of Hydrocarbons by ZSM-5 Zeolites with Different SiO_2/Al_2O_3 Ratios: A Combined FTIR and Gravimetric Study. *Applied Catalysis B: Environment.* 21: 243-258.

Jackson, S.D. Kelly, G.J. and Webb, G. (1998). Supported Metal Catalysts; Preparation, Characterisation, and Function. Part VI. Hydrogenolysis of Ethane, Propane, n-Butane and iso-Butane over Supported Platinum Catalysts. *Journal of Catalysis.* 176: 225-234.

Javanmardi, J., Nasrifar, K., Najibi, S. H. and Moshfeghian, M. (2005). Economic Evaluation of Natural Gas Hydrate as an Alternative for Natural Gas Transportation. *Applied Thermal Engineering* 25: 1708-1723.

Jeanette, S. (1980). *Zeolite Technology and Applications Recent Advances*. Park Ridge, NJ : Noyes Data Corp.

Jentys, A., Lugstein, A. and Vinek, H. (1997). Characterization of Metallic Species on Ni-and Co- containing ZSM-5 Catalysts-reduction Behavior and Catalytic Properties. *Zeolites.* 18 : 391-397.

Jeong, S., Fisher, K.J., Howe, R.F. and Willett, G.D. (1998). A Fourier Transform Mass Spectrometry Study of Ethane Oligomers in HMFI Zeolite. *Microporous and Mesoporous Materials.* 22: 369-377.

Jong, S.J. and Cheng, S. (1995). Reduction Behavior and Catalytic Properties of Cobalt Containing ZSM-5 zeolites. *Applied Catalysis A: General.* 126: 51-66.

Kanai, J. and Kawata, N. (1990). Coke Formation and Ageing of Galloalumino-silicate (ZSM-5 Type Zeolite). *Applied Catalysis.* 62: 141-150.

Kanai, J.,Martens, J.A. and Jacobs, P.A. (1992). On the Nature of the Active Sites for Ethylene Hydrogenation in Metal-free Zeolites. *Journal of Catalysis.* 133: 527-543.

Kaneko, K., Ohtani, K., Tsujikawa, Y. and Fuji, S. (2004). Utilization of the Cryogenic Exergy of LNG by a Mirror Gas-turbine. *Applied Energy* 79:355-369.

Karasuda, T. and Aika, K.I. (1997). Isotopic Oxygen Exchange between Dioxygen and MgO Catalysts for Oxidative Coupling of Methane. *Journal of Catalysis* 171: 439-448.

Keipert, O.P., Wolf, D., Schulz, P. and Baerns, M. (1995). Kinetics of Ethane Aromatization over A Gallium-Doped H-ZSM-5 Catalysts. *Applied Catalysis A: General*. 131: 347-365.

Kerby, M. C., Degnan, T. F., Marler, D. O. and Beck, J. S. (2005). Advanced Catalyst Technology and Applications for High Quality Fuels and Lubricants. *Catalysis Today*. 104: 55-63.

Keudell, A.V. and Jacob, W. (2004). Elementary Processes in Plasma-surface interaction: H-atom and Ion-induced Chemisorption of Methyl on Hydrocarbon Film Surfaces. *Progress in Surface Science.* 76: 21-54.

Kim, I., Kwak, C.H., Kim, J.S. and Ha, C.S. (2005). Ethylene Oligomerizations to Low-carbon Linear α-olefins by Structure Modulated Phenoxy-imine

Nickel(II) Complexes Combined with Aluminum Sesquichloride. *Applied Catalysis A: General.* 287: 98-107.

Kim, S.C., Kim, S.J. and Yu, E.Y. (1997). The Effect of Alkali Metal Salts on ZnO/α-Al_2O_3 and MnO_2 Catalysts for the Oxidative Coupling of Methane. *Applied Catalysis A: General.* 150:63-76.

Klinowski,J. and Barrie,P.J. (1988).*Recent Advances in Zeolite Science*. Amsterdam: Elsevier.

Koch, P.N., Mavris, D. and Mistree, F. (1998). *Multi-level, Partitioned Response Surfaces for Modeling Complex Systems.* American Institute of Aeronautics and Astronautics. AIAA-98-4958.

Kresnawahjuesa, O., Kuhl, G.H., Gorte, R.J. and Quierini, C.A. (2002). An Examination of Bronsted Acid Sites in H-[Fe]ZSM-5 for Olefin Oligomerization and Adsorption. *Journal of Catalysis.* 210:106-115.

Krische, M. J. (2005). A Brief Perspective on Catalysis from Its Origins and at the Threshold of the 21st Century. *Tetrahedron.* 61: 6169-6170.

Krishna, K. and Makkee, M. (2005). Coke Formation over Zeolites and CeO_2-Zeolites and Its Influence on Selective Catalytic Reduction of NO_x. *Applied Catalysis B: Environmental.* 59: 35-44.

Krishna, R. and Baur, R. (2003). Modelling Issues in Zeolite based Separation Processes. *Separation and Purification Technology*. 33: 213-254.

Kubacka, A., Wloch,E., Sulikowski, B., Valenzuela, R.X. and Corberan, V.C. (2000). Oxidative Dehydrogenation of Propane on Zeolite Catalysts. *Catalysis Today.* 61: 343-352.

Kucherov, A. V. , Slinkin, A. A., Kharson, M. S. , Bondarenko, T. N. and Minachev, K.M. (1989**)**. PART 3. Olefin Oligomerization and Aromatization on Parent and Dehydroxylated H-ZSM-5 :Formation of Radicals and Catalytic Activity of H-ZSM-5-type Zeolites in Unsaturated Hydrocarbon Conversions. *Journal of Molecular Catalysis.* 53 : 293-303.

Kus, S. and Taniewski, M. (2002b). The Effect of Some Impurities on the Basicity of MgO Tested by the Transformation of 2-butanol and on Its Catalytic Performance in Oxidative Coupling of Methane. *Fuel Processing Technology* 76 : 41-49.

Kus, S., Otremba, M. and Taniewski, M. (2003). The Catalytic Performance in Oxidative Coupling of Methane and the Surface Basicity of La_2O_3, Nd_2O_3, ZrO_2 and Nb_2O_5. *Fuel.* 82 : 1331-1338.

Kus, S., Otremba, M., Torz, A. and Taniewski, M. (2002). The Effect of Gas Atmosphere used in the Calcination of MgO on its Basicity and Catalytic Performance in Oxidative Coupling of Methane. *Applied Catalysis A: General.* 230: 263-270.

Kus, S., Otremba, M., Torz, A. and Taniewski, M. (2002a). Further Evidence of Responsibility of Impurities in MgO for Variability in its Basicity and Catalytic Performance in Oxidative Coupling of Methane. *Fuel.* 81: 1755-1760.

Kwak, B. S., Sachtler W. M. H. and Haag W. O. (1994).Catalytic Conversion of Propane to Aromatics: Effects of Adding Ga and/or Pt to HZSM-5. *Journal of Catalysis.*149:465-473.

Lacheen, H.S. and Iglesia, E. (2005). Stability, Structure and Oxidation State of Mo/H-ZSM-5 Catalysts During Reactions of CH_4 and CH_4-CO_2 Mixtures. *Journal of Catalysis.* 230: 173-185.

Lacombe, S., Geantet, C. and Mirodatos C. (1994). Oxidative Coupling of Methane over Lanthana Catalysts I. Identification and Role of Specific Active Sites. *Journal of Catalysis.* 151: 439-452.

Lacombe, S., Geantet, C. and Mirodatos, C. (1995). Oxidative Coupling of Methane over Lanthana Catalysts II. A Mechanistic Study Using Isotope Transient Kinectics. *Journal of Catalysis*. 155: 106-116.

Landi, G., Lisi, L. and Volta, J.C. (2004). Oxidation of Propane to Acrylic Acid over Vanadyl Pyrophosphate: Modifications of the Structural and Acid Properties during the Precursor Activation and Their Relationship with Catalytic Performances. *Journal of Molecular Catalysis A*. 222: 175-181.

Lange, J.P., Schoonebeek, R.J., Mercera, P.D.L. and Breukelen, F.W.V. (2005). Oxycracking of Hydrocarbons: Chemistry, Technology and Economics Potential. *Applied Catalysis A: General.* 283: 243-253.

Laosiripojana, N. and Assabumrungrat, S. (2005). Catalytic Dry Reforming of Methane over High Surface Area Ceria. *Applied Catalysis B : Environmental* 60 : 107-116.

Lebedeva, O., Chiou, W.A. and Sachtler, W.M.H. (1999). Metal Migration from Zeolites onto Iron Oxide: An Alternative to Hydrogen Spillover. *Journal of Catalysis*. 188. 365-374.

Lee, S.H.D., Applegate, D.V., Ahmed, S., Calderone, S.G. and Harvey, T.D. (2005). Hydrogen from Natural Gas: Part I-Autothermal Reforming in an Integrated Fuel Processor. *International Journal of Hydrogen Energy*. 30: 829-842.

Lee, J.H, Kim, J.G., Lee, J.K. and Kim J.H. (2003). NO Removal by CH_4 on Co-NaX-CO and Ag-NaX Catalysts in a Dual-bed System. *Catalysis Today*. 87: 35-42.

Lefferts, L., Seshan,K., Mojet, B.and Ommen, J.V. (2005). Non-conventional Oxidation Catalysis. *Catalysis Today*. 100: 63-69.

Li, C. (2003). Identifying the Isolated Transition Metal Ions/oxides in Molecular Sieves and on Oxides Supports by UV Resonance Raman Spectroscopy. *Journal of Catalysis.* 216 : 203-212.

Li, Y. and Armor, J.N. (1998). A Reaction Pathway for the Ammoxidation of Ethane and Ethylene over Co-ZSM-5 Catalyst. *Journal of Catalysis.* 176: 495-502.

Limtrakul, J., Nanok, T., Jungsuttiwong, S., Khongpracha, P. and Truong, T.N. (2001). Adsorption of Unsaturated Hydrocarbons on Zeolites: The Effects of the Zeolites Framework on Adsorption Properties of Ethylene. *Chemical Physics Letters.* 349: 161-166.

Lin, J.F. and Chou, C.C. (2002). The Response Surface Method and the Analysis of Mild Oxidational Wear. *Tribology International.* 35: 771-785.

Lintuluoto, M. and Nakamura, Y. (2004). Theoretical Study on the Adsorption of Methane on MgO and Li-doped MgO Surfaces. *Journal of Molecular Structure (Theochem).* 674: 207-212.

Liu, H., Li, Y., Shen, W., Bao, X. and Xu, Y. (2004a). Methane Dehydrogenation over Mo/HZSM-5 Catalysts in the Absence of Oxygen: Effects of Silanation in HZSM-5 Zeolite. *Catalysis Today.* 93-95: 65-73.

Liu, H.L., Lan, Y.W., and Cheng, Y.C. (2004b). Optimal Production of Sulphuric Acid by Thiobacillus Thiooxidans Using Response Surface Methodology. *Process Biochemistry.* 39: 1953-1961.

Liu, S., Wang, L., Ohnishi, R. and Ichikawa, M. (1999). Bifunctional Catalysis of Mo/HZSM-5 in the Dehydroaromatization of Methane to Benzene and Naphthalene XAFS/TG/DTA/MASS/FTIR Characterization and Supporting Effects. *Journal of Catalysis.* 181: 175-188.

Liu, Y. (1999). *Catalysts for Oxidative Dehydrogenation- Symyx Technologies.* (U.S. Patent 6,436,871).

Liu, Y. (2002). *Ni Catalysts and Methods for Alkane Dehydrogenation*. (U.S. Patent 6,417,422).

Lobree, L.J., Hwang, I.C., Reimer, J.A and Bell, A.T. (1999). Investigations of the State of Fe in H-ZSM-5. *Journal of Catalysis.* 186: 242-253.

Lonyi, F. and Valyon, J. (2001). On the interpretation of the NH_3-TPD patterns of H-ZSM-5 and H-mordenite. *Microporous and Mesoporous Materials.* 47: 293-301.

Lucas, A.D., Canizares, P. Duran, A. and Carrero, A. (1997). Coke Formation., Location, Nature and Regeneration on Dealuminated H-ZSM-5 Type Zeolites. *Applied Catalysis A: General.* 156: 299-317.

Lucas, A.D., Valverde, J.L., Canizares, P. and Rodriguez L. (1998). Partial Oxidation of Methane to Formaldehyde over W/HZSM-5 Catalysts. *Applied Catalysis A: General.* 172: 165-176.

Lunsford, J. H. (2000). Catalytic Conversion of Methane to More Useful Chemicals and Fuels: a Challenge for the 21st Century. *Catalysis Today.* 63: 165-174.

McDonald, M.A., Zarochak, M.F. and Graham, W.J. (1994).Effects of Pressure on the Oxyhydrochlorination of Methane. *Chemical Engineering Science.* 24: 4627-4637.

Maitra, A.M. (1993). Critical Performance Evaluation of Catalysts and Mechanistic Implications for Oxidative Coupling of Methane. *Applied Catalysis A: General.* 104: 11-59.

Maksimov, N.G., Selyutin, G.E., Anshits, A.G., Kondratenko, E.V. and Roguleva, V.G. (1998). The Influence of Defect Nature on Catalytic Performance of Li, Na-doped MgO, CaO and SrO in the Oxidative Coupling of Methane. *Catalysis Today*. 2: 279-281.

Mallens, E.P.J., Hoebink, J.H.B.J. and Marin, G.B. (1996). An Investigation of the Oxygen Pathways in the Oxidative Coupling of Methane over MgO-Based Catalysts. *Journal of Catalysis.* 160: 222-234.

Mao, R.L.V., Le, T.S., Fairbairn,M., Muntasar,A., Xiao, S. and Denes, G. (1999). ZSM-5 Zeoite with Enhanced Acidic Properties. *Applied Catalysis A*: *General.* 185: 41-52.

Marquis, S., Moissette, A., Vezin, H. And Bremard, C. (2005). Spontaneous Ionization and Electron Transfer of Polyaromatics by Sorption in ZSM-5 Zeolites. *C.R. Chimie.* (In Press).

Martin, G.A. and Mirodatos, C. (1995). Surface Chemistry in the Oxidative Coupling of Methane. *Fuel Processing Technology.* 42: 179-215.

Mayerhoff, Z.D.V.L., Roberto, I.C. and Franco, T.T. (2004). Purification of Xylose Reductase from Candida Mogii in Aqueous Two-phase Systems. *Biochemical Engineering Journal.* 18: 217-223.

Minchev, C., Zubkov, S.A, Valtchev, V., Minkov,V., Micheva, N. and Kanazirev, V. (1994). Nature of the Active Sites and Catalytic Activity of SAPO-5 Synthesized in the Presence of Nickel Cations. *Applied Catalysis A: General.* 119: 195-204.

Mleczko, L. and Baerns, M. (1995). Catalytic Oxidative Coupling of Methane – Reaction Engineering Aspects and Process Schemes. *Fuel Processing Technolog.* 42: 217-248.

Montes, A. and Giannetto, G. (2000). A New Way to Obtain Acid or Bifunctional Catalysts V. Consideration on Bifunctionality of the Propane Aromatization Reaction Over [Ga, Al]-ZSM-5 Catalysts. *Applied Catalysis A: General.* 197: 31-39.

Mulla, S.A.R. and Choudhary, V.R. (2004). Oxidative Conversion of Ethane to Ethylene over Supported SrO-promoted Er_2O_3 Catalyst. *Journal of Molecular Catalysis A: Chemical.* 223: 259-262.

Murakami, Y., Iijima, A. and Ward, J. W. (1986). *New Developments in Zeolite Science and Technology.* Amsterdam : Elsevier.

Nagamori, Y. and Kawase, M. (1998). Converting Light Hydrocarbons Containing Olefins to Aromatics (Alpha Process). *Microporous and Mesoporous Materials.* 21: 439-445.

Nascimento, M.A.C. (1999). Computer Simulations of the Adsorption Process of Light Alkanes in High-silica Zeolites. *Journal of Molecular Structure (Theochem).* 464: 239-247.

Neyestanaki, A.K. and Kumar, N. and Lindfors, L.E. (1995). Catalytic Combustion of Propane and Natural Gas over Cu and Pd Modified ZSM Zeolite Catalysts. *Applied Catalysis B: Environment.* 7: 95-111.

Nicolaides, C.P., Scurell, M.S. and Semano, P.M. (2003). Nickel Silica-alumina Catalysts for Ethene Oligomerization-control of the Selectivity to 1- alkene Products. *Applied Catalysis A: General.* 245: 43-53.

Nkosi, B., Ng, F.T.T. and Rempel, G.L. (1997a). The Oligomerization of 1-butene Using NaY Zeolite Ion-exchanged with Different Nickel Precursor Salts. *Applied Catalysis A: General.* 161: 153-166.

Nkosi,B., Ng, F.T.T. and Rempel, G.L. (1997b). The Oligomerization of Butenes with Partially Alkali Exchange NiNaY Zeolite Catalysts. *Applied Catalysis A: General.* 158 : 225-241.

Nogales, J.M.R., Roura, E. and Contreras, E. (2005). Biosynthesis of Ethyl Butyrate Using Immobilized Lipase: A Statistical Approach. *Process Biochemistry.* 40: 63-68.

Nowinska, K., Waclaw, A. and Izbinska, A. (2003). Propane Oxydehydrogenation over Transition Metal Modified Zeolite ZSM-5. *Applied Catalysis A: General.* 243: 225-236.

Ohman, L.O., Ganemi B., Bjornbom E., Rahkamaa K., Keiski R.L., and Paul J. (2002). Catalyst Preparation Through Ion-exchange of Zeolite Cu-, Ni-, Pd-, CuNi- and CuPd-ZSM-5. *Material Chemistry and Physics.* 73: 263-267.

Okamoto Y.(1997). Preparation and Characterization of Zeolite-supported Molybdenum and Cobalt-molybdenum Sulfide Catalysts. *Catalysis Today.*39: 45-59.

Pak, S., Qiu, P. and Lunsford, J.H. (1998). Elemenatry Reactions in the Oxidative Coupling of Methane over $Mn/Na_2WO_4/SiO_2$ and $Mn/Na_2WO_4/MgO$ Catalysts. *Journal of Catalysis.* 179: 222-230.

Panjan, W. and Limtrakul, J. (2003). The Influence of the Framework on Adsorption Properties of Ethylene/H-ZSM-5 System: an ONIOM Study. *Journal of Molecular Structure.* 654: 35-45.

Panov, G.I., Uriarte,A.K., Rodkin, M.A. and Sobolev, V. (1998). Generation of Active Oxygen Species on Solid Surfaces. Opportunity for Novel Oxidation Technologies over Zeolites. *Catalysis Today.* 41 :365-385.

Pareja,P., Molina,S., Amariglio, A. and Amariglio, H. (1998). Isothermal Conversion of Methane into Higher Hydrocarbons and Hydrogen by a Two-step Reaction Sequence Involving a Rhodium Catalyst. *Applied Catalysis A: General.* 168: 289-305.

Park, K. and Ahn, J.H. (2004). Design of Experiment Considering Two-way Interactions and Its Application to Injection Molding Processes with Numerical Analysis. *Journal of Materials Processing Technology.* 146: 221-227.

Patel, V.J., Tendulkar,S.R., Chattoo, B.B. (2004). Bioprocess Development for the Production of an Antifungal Molecule by *Bacillus licheniformis* BC98. *Journal of Bioscience and Bioengineering*. 98: 231-235.

Pathirana, C.L. and Shahidi, F. (2005). Optimization of Extraction of Phenolic Compounds from Wheat Using Response Surface Methodology. *Food Chemistry.* 93: 47-56.

Pérez, J., García, J. M., Kapteijn, F., Illán-Gómez , M. J., Ribera, A., Salinas, C.and Moulijn, J.A. (2000). Dual-bedCatalytic System for NO_x–N_2O Removal: A Practical Application for Lean-burn deNO_x HC-SCR . *Applied Catalysis B: Environmental* 25:191-203.

Pieters, W. J. M., Conner, W.C. and Carlson, E. J. The Oxyhydrochlorination of Methane on Fumed Silica - Based Cu^{+1}, K, La Catalysts: I. Catalyst Synthesis. *Applied Catalysis*. 11: 35-48.

Pinarello, G., Pisani, C., Ercole, A.D., Chiesa, M., Paganini, M.C., Giamello, E., Diwald, O. (2001). O^- radical ions on MgO as a Tool to Unravel Structure and Location of Ionic Vacancies at the Surface of Oxides: a Coupled Experimental and Theoretical Investigation. *Surface Science.* 494: 95-110.

Pinto, R.R., Borges, P., Lemos M., Lemos, F., Vedrine, J.C., Derouane, E.G. and Ribeiro, F.R. (2005). Correlating NH_3-TPD and H MAS NMR Measurements of Zeolite Acidity: Proposal of An Acidity Scale. *Applied Catalysis A: General.* 284: 39-46.

Ponec, V. (1998). Forty Years in CATALYSIS: What Have We Learned? *Journal of Molecular Catalysis A: Chemical.* 133: 221-239.

Pradhan, A.R., Wu, J.F., Jong, S.J., Chen, W.H., Tsai, T.C. and Liu, S.B. (1997). Influences of Zeolites Structure on Formation and Location of Coke: A ^{129}Xe and ^{13}C CP-MAS NMR Study. *Applied Catalysis A: General.* 159: 187-209.

Praserthdam, P. and Ayutthaya, S.I.N. (2004). Roles of NO and O_2 on Coke Deposition and Removal over Cu-ZSM-5. *Catalysis Today.* 97: 137-143.

Qian, L. and Yan, Z.F. (2001). Micropore Modification of Zeolites with Transition-Metal Oxides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 180: 311-316.

Qian, Y., Zhao, W. and Huang, J. (2004). Synthesis, Crystal Structure, and Olefin Oligomerization Activity of Neutral Arylnickel (II) phosphine Catalyst with 2-oxazolinylphenolato N-O Chelate Ligand. *Inorganic Chemistry Communications.* 7: 459-461.

Rabo, J.A. (1976). *Zeolite Chemistry and Catalysis.* Washington, D.C. American Chemical Society.

Ramasamy, A.V. (2003). Catalysts Selectivity: Shape Selective Catalysis over Zeolites. *Bulletin of the Catalysis Society of India.* 2: 140-156.

Rezzoug, S.A., Boutekedjiret, C. and Allaf, K. (2005). Optimization of Operating Conditions of Rosemary Essential Oil Extraction by a Fast Controlled Pressure Drop Process Using Response Surface Methodology. *Journal of Food Engineering.* 71: 9-17.

Ribeiro, F. R., Alvarez, F., Henriques, C., Lemos, F., Lopes, J. M. and Ribeiro, M. F. (1995). Sructure-Activity Relationship in Zeolites. *Journal of Molecular Catalysis A: Chemical.* 96: 245-270.

Rice, M.J., Chakraborty, A.K. and Bell, A. (2000). Site Availability and Competitive Sitting of Divalent Metal Cations in ZSM-5. *Journal of Catalysis.* 194: 278-285.

Rice, R.W. and Keptner, D.C. (2004). The effect of Bimetallic Catalyst Preparation and Treatment on Behavior for Propane Hydrogenolysis. *Applied Catalysis A: General.* 262 : 233-239.

Richardson, R.N., Scurlock, R.G. and Tavner, A.C.R. (1994). Cryogenic Engineering of High Temperature Superconductors Below 77K. *Cryogenics*. 35: 387-391.

Roland, U., Braunschweig, T. and Roessner, F. (1997). On the Nature of Spilt-over Hydrogen. *Journal of Molecular Catalysis A: Chemical.* 127 : 61-84.

Roldan, R., Romero, F.J., Sanchidrian, C.J., Marinas, J.M. and Gomez, J.P. (2005). Influence of Acidity and Pore Geometry on the Product Distribution in the Hydroisomerization of Light Paraffins on Zeolites. *Applied Catalysis A: General.* 288: 104-115.

Royer, S., Alamdari, H., Duprez, D. and Kaliaguine, S. (2005). Oxygen Storage Capacity of La1-x A'xBO$_3$ Perovskites (with A'=Sr, Ce; B=Co, Mn)-Relation With Catalytic Activity in the CH$_4$ Oxidation Reaction. *Applied Catalysis B: Environmental.* 58 : 273-288.

Sahoo, S.K., Viswanadham, N., Ray, N., Gupta, J.K. and Singh, I.D. (2001). Studies on Acidity, Activity and Coke Deactivation of ZSM-5 During n-heptane Aromatization. *Applied Catalysis A: General.* 205: 1-10.

Samarth, R.D., Chen, S.Y. and Dooley, K.M. (1994). Dual-bed Strategies to Improve Hydrocarbon Yield in the Oxidative Coupling of Methane. *Applied Catalysis B: Environmental.* 5: 71-88.

Sano,T., Uno,Y., Wang, Z.B. Ann, C.H and Soga, K. (1999). Realumination of Dealuminated HZSM-5 Zeolites by Acid Treatment and Their Catalytic Properties, *Microporous and Mesoporous Materials. 31*: 89-95.

Sarioglan, A., Senatalar, A.E., Savaschi, O.T. and Taarit, Y.B. (2004). The Effect of Dealumination on the Apparent and Actual Rates of Aromatization of Methane over MFI-supported Molybdenum Catalysts. *Journal of Catalysis*. 226 : 210-214.

Schuurman, Y., Ducarme, V., Li, W., Mirodatos, C. and Martin, G.A. (1997). Low Temperature Oxidative Dehydrogenation of Ethane over Catalysts Based on Group VIII Metals. *Applied Catalysis A: General.* 163: 227-235.

Schwarz, S., Kojima,M., and Connor, C.T.O. (1989). Effect of Silicon-to-Aluminium Ratio and Synthesis Time on High-pressure Olefin Oligomerization over ZSM-5. *Applied Catalysis*. 56: 263-280.

Senkan, S. *Production of Higher Molecular Weight Hydrocarbons from Methane*. U.S. Patent 4,714,796. 1987.

Serrano, V.G., Garcia, C.M.G. and Martin, M.L.G. (2001). Nitrogen Adsorption Isotherms on Carbonaceous Materials. Comparison of BET and Langmuir Surface Areas. *Powder Technology.*116: 103-108.

Sethuraman, R., Bakhsi, N.N., Katikaneni, S. and Idem, R.O. (2001). Production of C_4 Hydrocarbons from Fischer-Tropsch Synthesis in a Follow Bed Reactor Consisting of Co-Ni-ZrO_2 and Sulfated-ZrO_2 Catalysts Beds. *Fuel Processing Technology. 73*: 197-222.

Shpiro, E. S., Shevchenko, D. P., Tkachenko, O. P. and Dmitriev, R. V. (1994). Platinum Promoting Effects in Pt/Ga zeolite Catalysts of Lower Alkane Aromatization. I. Ga and Pt Electronic States, Dispersion and Distribution in Zeolite Crystals in Dependence of Preparation Techniques. Dynamic Effects Caused by Reaction Mixture. *Applied Catalysis A: General. 107: 147-164.*

Siddiq, T.A. (2002). Natural Gas Reserves/ Total Energy Consumption: A Useful New Ratio for Addressing Global Climate Change Concerns. *Energy Policy.* 30: 1145-1149.

Sierraalta, A., Afiez, R. and Brussin, M-R. (2002). Theoretical Study of NO_2 Adsorption on a Transition-Metal Zeolite Model. *Journal of Catalysis*. 203: 107-114.

Sinev, M.Y. (1995). Kinetic Modeling of Heterogeneous-homogeneous Radical Processes of the Partial Oxidation of Low Paraffins. *Catalysis Today*. 24: 389-393.

Sinev, M.Y. (2003). Free Radicals in Catalytic Oxidation of Light Alkanes: Kinetic and Thermochemical Aspects. *Journal of Catalysis*. 216: 468-476.

Sinev, M.Y., Fattakhova, Z.T., Tulenin, Y.P., Stennikov, P.S., Vislovskii, V.P. (2003). Hydrogen Formation During Dehydrogenation of C_2-C_4 Alkanes in The Presence of Oxygen: Oxidative or non-Oxidative? *Catalysis Today.* 81: 107-116.

Sinev, M.Y. (2003). Elementary Steps of Radical-surface Interactions in Oxidative Coupling of Methane. *Catalysis Today.* 13: 561-564.

Sing, K. (2001). The Use of Nitrogen Adsorption for the Characterization of Porous Materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 187-188: 3-9.

Slinkin, A.A. and Kucherov, A.V. (1997). New Strategy of Creation of Local Catalytic Sites in Definite Electronic and Coordination States. *Catalysis Today.* 36: 485-496.

Solymosi, F. and Szoke, A. (1998). Conversion of Ethane into Benzene on Mo_2C/ZSM-5 Catalyst. *Applied Catalysis A: General.* 166: 225-235.

Solymosi, F., Cserenyi, J., Szoke, A., Bansagi, T. and Oszko, A. (1997). Aromatization of Methane over Supported and Unsupported Mo-Based Catalysts. *Journal of Catalysis.*165: 150-161.

Somorjai, G.A. and McCrea, K. (2001). Roadmap for Catalysis Science in the 21st Century: A Personal View of Building the Future on Past and Present Accomplishments. *Applied Catalysis A: General.* 222: 3-18.

Spivey, J. J. (2005). Catalysis in the Development of Clean Energy Technologies. *Catalysis Today*. 100: 171-180.

Stefaniak, W. Goworek, J. and Bilinski, B. (2003). Pore Size Analysis by Nitrogen Adsorption and Thermal Desorption. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. 214: 231-237.

Stockenhuber, M., Joyner, R.W., Dixon, J.M., Hudson, M.J. and Grubert, G. (2001). Transition Metal Containing Mesoporous Silicas-Redox Properties, Structure and Catalytic Activity. *Microporous and Mesoporous Materials*. 44-45: 367-375.

Stocker, M. (1996). X-Ray Photoelectron Spectroscopy on Zeolites and Related Materials. *Microporous Materials*. 6 : 235- 257.

Stocker, M. (2005). Gas Phase Catalysis by Zeolites. *Microporous and Mesoporous Materials*. 82 (In press).

Taguchi, A. and Schuth, F. (2005). Ordered Mesoporous Materials in Catalysis. *Microporous and Mesoporous Materials*. 77: 1-45.

Tan, P.L., Leung, Y.L., Lai, S.Y. and Au, C.T. (2002). The Effect of Calcinations Temperature on the Catalytic Performance of 2 wt.% Mo/HZSM-5 in Methane Aromatization. *Applied Catalysis A: General*. 228: 115-125.

Tan, P.L., Wong, K.W., Au, C.T. and Lai, S.Y. (2003). Effects of Co-fed O_2 and CO_2 on the Deactivation of Mo/HZSM-5 for Methane Aromatization. *Applied Catalysis A: General*. 253: 305-315.

Tang, X., Sun, W.H., Gao, T., Hou, J., Chen, J. and Chen, W. (2005). Nickel (II) Complexes Bearing 2-ethylcarboxylate-6-iminopyridl Ligands: Synthesis, Structures and Their Catalytic Behavior for Ethylene Oligomerization and Polymerization. *Journal of Organometallic Chemistry*. 690: 1570-1580.

Tanyilidizi, M., Ozer, D. and Elibot, M. (2005). Optimization of α-amylase Production by *Bacillus* sp. Using Response Surface Methodology. *Process Biochemistry*. 40: 2291-2296.

Thomas, S. and Dawe, R.A. (2003). Review of Ways to Transport Natural Gas Energy from Countries which Do Not Need the Gas For Domestic Use. *Energy*. 28: 1461-1477.

Timmons,R.B., He, Y., Jang, W.L. (1992).*Zeolite Catalyzed Conversion of Acetylene*. (U.S. Patent 5,118,893).

Tran, M.T. , Gnep, N.S. Szabo, G., Guisnet, M. (1998). Influence of the Calcination Temperature on the Acidic and Catalytic Properties of Sulphated Zirconia. *Applied Catalysis A: General.* 171: 207-217.

Traykova, M., Davidova, N., Tsaih, J.S. and Weiss, A.H. (1998). Oxidative Coupling of Methane-transition from Reaction to Transport Control over La_2O_3/MgO Catalyst. *Applied Catalysis A: General.* 169: 237-247.

Triantafillidis,C.S., Vlessidis,A.G., Nalbandian, L. and Evmiridis, N.P. (2001). Effect of the Degree and Type of the Dealumination Method on the Structural, Compositional and Acidic Characteristics of HZSM-5 Zeolites, *Microporous and Mesoporous Materials.* 47: 369-388.

Tye, C.T.T., Mohamed, A.R. and Subhash, B. (2002). Modeling of Catalytic Reactor for Oxidative Coupling of Methane Using La_2O_3/CaO Catalyst. *Chemical Enginnering Journal.* 87: 49-59.

Tynjala, P. and Pakkanen, T.T. (1998). Modification of ZSM-5 Zeolite with Trimethyl Phosphate Part 1. Structure and Acidity. *Microporous and Mesoporous Materials.* 20: 363-369.

Vaarkamp, M., Miller, J.T., Modica, F.S. and Koningsberger, D.C. (1996). On the Relation between Particle Morphology, Structure of the Metal-Support

Interface, and Catalytic Properties of Pt/γ-Al_2O_3. *Journal of Catalysis.* 163: 294-305.

Vereshchagin, S.N., Dugaev, K.P., Kirik, N.P., Shishkina, N.N. and A.G.Anshits. (1995). Conversion of Hydrocarbons over Zeolites and Phosphoric Acid, *Catalysis Today.* 24: 349-355.

Vereshchagin, S.N., Shishkina, N.N. and Anshits, A.G. (1998). Oxidative and Nonoxidative Conversion of C_2 hydrocarbons on ZSM-5. *Catalysis Today.* 42: 303-310.

Viswanadham, N., Muralidhar, G. and Rao, T.S.R.P. (2004). Cracking and Aromatization Properties of Some Metal Modified ZSM-5 Catalysts For Light Alkane Conversions. *Journal of Molecular Catalysis A: Chemical.* 223: 269-274.

Vislovskiy,V.P., Suleimanov, T. E., Sinev, M.Y., Tulenin,Y.P, Margolis,L.Y and Corberán, V.C. (2000). On the Role of Heterogeneous and Homogeneous Processes in Oxidative Dehydrogenation of C_3-C_4 Alkanes. *Catalysis Today.* 61: 287-293.

Vohra, A. and Satyanarayana,T. (2002). Statistical Optimization of the Medium Components by Response Surface Methodology to Enhance Phytase Production by *Pichia Anomala. Process Biochemistry.* 37: 999-1004.

Vosloo, A.C. (2001). Fischer-Tropsch: a Futuristic View. *Fuel Processing Technology.* 71: 149-155.

Wang, D.Z., Lu, X.D., Dou, X.Y., Li, W.B. and Yang, C.H. (1990). Effect of Acidity of HZSM-5 Type Zeolite on Conversion of Alkenes to Gasoline and Aromatics. *Applied Catalysis.* 59: 75-88.

Wang, H., Cong, Y. and Yang, W. (2005). Oxidative Coupling of Methane in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Tubular Membrane Reactors. *Catalysis Today.* (In Press).

Wang, L., Xu, Y., Wong, S.T., Cui, W. and Guo, X. (1996). Activity and Stability enchancement of Mo/HZSM-5-based Catalysts for Methane Non-Oxidative Transformation to Aromatics and C_2 Hydrocarbons: Effect of Additives and Pretreatment Conditions. *Applied Catalysis A: General.* 152: 173-182.

Wang, Y.X. and Lu, Z.X. (2005). Optimization of Processing Parameters for the Mycelial Growth and Extracellular Polysaccharide Production by *Boletus* spp. ACCC 50328. *Process Biochemistry.* 40: 1043-1051.

Weckhuysen, B.M., Wang, D., Rosynek, M.P. and Lunsford, J.H. (1998). Conversion of Methane to Benzene over Transition Metal Ion ZSM-5 Zeolites. I. Catalytic Characterization. *Journal of Catalysis.* 175: 338-346.

Weitkamp, J. (1998). *Zeolites and Related Microporous Materials: State of the Art.* Amsterdam : Elsevier.

Weitkamp, J. (2000). Zeolites and Catalysis. *Solid State Ionics.* 131: 175-188.

Wilhelm, D.J., Simbeck, D.R., Karp, A.D. and Dickenson, R.L. (2001). Syngas Production for Gas-to-Liquids Applications: Technologies, Issues and Outlook. *Fuel Processing Technology.* 71: 139-148.

Woolery, G.L., Kuehl, G. H., Timken, H. C., Chester, A. W. and Vartuli, J. C. (1997).On the nature of framework Brønsted and Lewis acid sites in ZSM-5. *Zeolites*. 19: 288-296.

Wu, T., Yan, Q. and Wan, H. (2005). Partial Oxidation of Methane to Hydrogen and Carbon Monoxide over a Ni/TiO_2 Catalyst. *Journal of Molecular Catalysis A: Chemical.* 226: 41-48.

Xing, E., Mi, Z., Xin, C., Wang, L. and Zhang, X. (2005). Endo- to Exo-Isomerization of Tetrahydrodicyclopentadiena Catalyzed by Commercially

Available Zeolites. *Journal of Molecular Catalysis A: Chemical.* 231: 161-167.

Xu, Y., Bao, X. and Lin, L. (2003). Direct Conversion of Methane under Nonoxidative Conditions. *Journal of Catalysis.* 216. 386-395.

Yagi, F., Kanai, R., Wakamatsu, S., Kajiyama, R., Suchiro, Y. and Shimura, M. (2005). Development of Synthesis Gas Production Catalyst and Process. *Catalysis Today.* 104: 2-6.

Yarlagadda, P., Lund, C.R.F. and Ruckenstein, E. (1990). Oligomerization of Ethene and Propene over Composite Zeolite Catalysts. *Applied Catalysis.* 62 : 125-139.

Yin, C., Zhao, R. and Liu, C. (2003). Hydrotreating of Cracked Naphtha over Ni/HZSM-5 Catalyst. *Energy & Fuels.* 17: 1356-1359.

Yin, C., Zhao, R. and Liu, C. (2005). Transformation of Olefin over Ni/HZSM-5 Catalyst. *Fuel.* 84: 701-706.

Yoo, J.S. (1998). Selective Gas-Phase Oxidation at Oxide Nanoparticles on Microporous Materials. *Catalysis Today.* 41: 409-432.

Yoshizawa, K. (2002). Theoretical Study on Kinetic Isotope Effects in the C-H bond Activation of Alkanes by Iron-oxo-complexes. *Coordination Chemistry Reviews.* 226: 251-259.

Yuan, S.P., Wang, J.G., Li, Y.W. and Peng, S.Y. (2002). Theoretical Studies on the Properties of Acid Site in Isomorphously Substituted ZSM-5. *Journal of Molecular Catalysis A: Chemical.* 178: 267-274.

Zaera, F. (2002). Selectivity in Hydrocarbon Catalytic Reforming: a Surface Chemistry perspective. *Applied Catalysis A: General.* 229: 75-91.

Zaman, J. (1997). Oxidative Processes in Natural Gas Conversion. *Fuel Processing Technology.* 58 : 61-81.

Zhang, A., Nakamura, I. and Fujimoto, K. (1997). A New Probe Reaction for Studying the Hydrogen Spillover Phenomenon. *Journal of Catalysis.* 168: 328-333.

Zhang, X., Gong, Y., Yu, G. and Xie, Y. (2002). Oxygen Species on NiO/Al_2O_3 and their Reactivities. *Journal of Molecular Catalysis A: Chemical.* 180: 293-298.

Zhang, X., Liu, J., Jing, Y. and Xie, Y. (2003). Support Effects on the Catalytic Behavior of NiO/Al_2O_3 for Oxidative Dehydrogenation of Ethane to Ethylene. *Applied Catalysis A: General.* 240: 143-150.

Zhu, J., Rahuman , M.S.M.M., Ommen, J.G.V. and L. Lefferts,L. (2004). Dual Catalyst Bed Concept for Catalytic Partial Oxidation of Methane to Synthesis Gas. *Applied Catalysis A: General.* 259: 95-100.

Zhu, J.Z., Ommen, J.G.V. and Lefferts, L. (2004). Reaction Scheme of Partial Oxidation of Methane to Synthesis Gas over Ytrium-stabilized Zirconia. *Journal of Catalysis.* 225: 388-397.

Zhu, X., Liu, S., Song, Y. and Xu, L. (2005). Catalytic Cracking of C_4 Alkenes to Propene and Ethene: Influences of Zeolites Pore Structures and Si/Al_2 Ratios. *Applied Catalysis A: General* (In press).