NICKEL OXIDE BASED CATALYSTS FOR THE SIMULTANEOUS
REACTIONS OF METHANATION AND DESULFURIZATION

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To my beloved father, mother, brothers and sisters,

who set me on my path.

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ABSTRACT

Malaysian crude natural gas is categorized as a sour gas due to the contamination of carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Recently, the removal of these sour gases via chemical conversion technique becomes the most promising technique. The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gases to be applicable in gas industry. The advantage of catalytic technology is the utilization of CO_2 present in the production of methane gas. Supported mixed metal oxide catalysts were prepared by wetness impregnation method for the in-situ reactions of H_2S desulfurization and CO_2 methanation from ambient temperature up to 300^oC. Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 and Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 catalysts were revealed as the most potential resulted from the catalytic activity screening by Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC). Results showed that the conversion of H_2S to elemental sulfur over the catalysts was achieved 100% even around 250^oC. Methanation of CO_2 in the presence of H_2S yielded 2.9% of CH_4 over Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 catalyst and 6.1% of CH_4 over Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 catalyst at maximum studied temperature of 300^oC. X-ray Photoelectron Spectroscopy (XPS) revealed Ni_2O_3 and Fe_3O_4 as the surface active components on the Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 catalyst, while Ni_2O_3 and Co_3O_4 on the Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 catalyst. X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) showed that the supported catalysts are amorphous in structure. Results from Energy Dispersive X-ray Analysis (EDX) indicated the presence of 2.7% and 0.9% of sulfur on the spent Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 and Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 catalysts, respectively. There was 5.5% reduction of surface area over the spent Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 catalyst characterized by Nitrogen Adsorption analysis. Meanwhile, there was 8.6% increment of surface area over the spent Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 catalyst, which would explain the dramatic increased of catalytic performance over this catalyst at maximum studied temperature of 300^oC. Characterization by FTIR and Thermogravimetry Analysis-Differential Thermal Analysis (TGA-DTA) revealed the existence of residue of nitrate and surface hydroxyl compounds on the catalysts. The aim to obtain high H_2S desulfurization rate at low temperature was achieved. However, improvement is still needed for the CO_2 methanation reaction at low temperature in the presence of H_2S.

ABSTRAK

Gas asli Malaysia tergolong sebagai gas masam disebabkan kewujudan gas karbon dioksida (CO_2) dan hidrogen sulfida (H_2S). Kebelakangan ini, penyingkiran gas-gas masam ini melalui kaedah penukaran kimia merupakan kaedah yang paling berkesan. Pembangunan mangkin baru ini bertujuan untuk mencapai peratus penukaran gas masam yang tinggi pada suhu yang sangat rendah, supaya dapat diaplikasikan di dalam industri gas asli. Kebaikan teknologi pemangkinan adalah menukarkan gas CO_2 yang sedia ada untuk penghasilan gas metana. Mangkin yang terdiri daripada campuran logam oksida berpenyokong disediakan dengan cara *wetness impregnation* untuk tindak balas penyahsulfuran H_2S dan metanasi CO_2 secara *in-situ* dari suhu bilik hingga 300°C. Mangkin Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 dan Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 ditentukan sebagai mangkin yang paling berpotensi hasil daripada ujian aktiviti pemangkinan dengan menggunakan FTIR dan GC. Hasil ujian menunjukkan penyahsulfuran H_2S mencapai 100% pada suhu sekitar 250°C. Tindak balas metanasi CO_2 dalam kehadiran H_2S menghasilkan 2.9% CH_4 dengan menggunakan mangkin Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 dan 6.1% CH_4 dengan menggunakan mangkin Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 pada suhu ujian maksimum 300°C. XPS dapat mengesan Ni_2O_3 dan Fe_3O_4 sebagai spesies permukaan yang aktif pada mangkin Fe/ Co/ Ni (10: 30: 60)-Al_2O_3. Di samping itu, Ni_2O_3 and Co_3O_4 dikesan sebagai spesies aktif pada mangkin Pr/ Co/ Ni (5: 35: 60)-Al_2O_3. Keputusan XRD dan FESEM mempamerkan struktur amorfus pada kedua-dua mangkin ini. Analisis EDX pada mangkin Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 dan Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 yang selepas ujian menunjukkan kehadiran sulfur sebanyak 2.7% dan 0.9% masing-masing. Daripada analisis Penjerapan Nitrogen, didapati sebanyak 5.5% penurunan pada luas permukaan mangkin Fe/ Co/ Ni (10: 30: 60)-Al_2O_3 selepas ujian. Peningkatan luas permukaan sebanyak 8.6% berlaku pada mangkin Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 selepas ujian. Fenomena ini mungkin menerangkan peningkatan aktiviti pemangkinan secara mendadak oleh mangkin Pr/ Co/ Ni (5: 35: 60)-Al_2O_3 pada suhu tindak balas 300°C. Pencirian mangkin menggunakan FTIR dan TGA-DTA menunjukkan bahawa masih terdapat kehadiran sisa-sisa nitrat dan hidroksi pada kedua-dua mangkin ini. Tujuan untuk mendapatkan peratus penyingkiran gas H_2S yang tinggi pada suhu rendah telah dicapai. Walaubagaimanapun, usaha masih diperlukan untuk meningkatkan tindak balas metanasi pada suhu rendah dengan kehadiran H_2S.

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LIST OF ABBREVIATIONS

ABS — Absorbance

BET — Brunnauer, Emmet and Teller

BJH — Barret-Joyner-Halenda

Btu — British thermal unit

c — Cubic

cf — Cubic feet

CHA — Concentric hemispherical analyzer

Cu Kα — X-ray diffraction from Copper K energy levels rate of conversion (percentage)

d — Pore diameter

DTA — Differential Thermal Analysis

E_b — Binding energy

E_k — Kinetic energy

E_{so} — Spinning orbital energy

EDX — Energy Dispersive X-ray Analysis

ESR — Electron Spin Resonance

eV — Electronvolt

fcc — Face-centered cubic

FESEM — Field Emission Scanning Electron Microscope

FID — Flame Ionization Detector

FTIR — Fourier Transform Infrared

FWHM — Full width half maximum

GC — Gas Chromatography

ΔH — Enthalpy change

h — Hexagonal

hr — Hour

hν	- Photon's energy
IUPAC	- International Union of Pure and Applied Chemistry
LNG	- Liquefied Natural Gas
m	- Monoclinic
MgKα	- X-ray diffraction from Magnesium K energy levels rate of conversion (percentage)
MS	- Mass Spectroscopy
P/P_o	- Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure P_o of the adsorbate at the temperature where the isotherm is measured
PDF	- Powder Diffraction File
ppm	- Part per million
SMSI	- Strong metal support interaction
tcf	- Trillion cubic feet
TGA	- Thermogravimetry Analysis
XPS	- X-ray Photoelectron Spectroscopy
XRD	- X-ray Diffraction
α_0	- Cell constant
θ	- Half angle of diffraction beam
λ	- Wavelength

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CHAPTER I

INTRODUCTION

1.1   Natural Gas

The principal hydrocarbon component of natural gas is methane. In many natural gas deposits, methane makes up 80 to 90 percent of the gas. Natural gas may contain other small hydrocarbon molecules such as ethane, propane, butane, pentane, and hexane. Besides these hydrocarbons, it may also comprise inorganic compounds such as nitrogen, helium, carbon dioxide and hydrogen sulfide. Natural gas is an ideal fuel. It requires minimal processing before use and has the highest calorific value of any fossil fuel.

Malaysia has the world's 13th largest natural gas reserves and 24th largest crude oil reserves. Malaysia is also the world's third largest producer of Liquefied Natural Gas (LNG) with production capacity of 23 million metric ton per year. Our country is important to world energy markets because of its 75 trillion cubic feet (tcf) of natural gas reserves and its net oil exports of over 940,000 barrels per day. Natural gas consumption in 2002 was estimated at 1.0 tcf, with LNG exports of around 0.7 tcf (mostly to Japan, South Korea and Taiwan) (Malaysia Oil and Gas, 2007).

Since natural gas contains no mineral, no ash residue is produced upon combustion, making it a cleaner fuel. Natural gas as the cleanest of the fossil fuels is second only to hydro and renewable energy resources in environmental friendliness.

Due to its gaseous state, it mixes with oxygen easily for more efficient combustion. Gas is the most thermally efficient fuel when used in combined cycle gas turbine power plants, which are in turn the most competitive with regard to expense, speed of construction, reduced maintenance and overall operability. According to International Energy Agency forecasts, power generation in the Organization for Economic Co-operation and Development Pacific (Japan, Korea, Australia and New Zealand), China and East and South Asia (Brunei, Indonesia, Taiwan, South Korea, Malaysia, Philippines, Singapore, Vietnam and Thailand; Bangladesh, India and Pakistan) will by 2020 see natural gas growing up by 113%, coal by 83% and oil consumption rising by just 15% (Mueller, 2004a). Natural gas fueled power plants are the preferred source of electrical energy. This is by considering the limited availability of hydro and other renewable power, coal fueled power generation and growing worries over nuclear plant safety.

It is expected that total investment requirements in the gas sector will reach $3.1 trillion, of which exploration and development will account for 55%, or $1.7 trillion. Upstream gas investment will continue to be concentrated in Australia, Indonesia and Malaysia, all of which have large proven reserves. Innovation will bring previously inaccessible natural gas reserves to market, thereby tending to lower the cost and improve the competitiveness of gas (Mueller, 2004b).

1.2 Research Background and Problem Statement

Natural gas is combustible and gives a great deal of power upon consumption. Natural gas is the future energy resource for Malaysia and this is ensured by Malaysia large reserves and further strength by the existence of huge gas reserves in the nearby countries (Md. Yasin, 1987). However, the gas often contains the other light alkanes and a variety of inorganic compounds, including hydrogen sulfide (H_2S), carbon dioxide (CO_2), helium (He) and hydrogen (H_2). The composition of a natural gas as it comes from the well varies from one location to another.

Table 1.1 shows the chemical composition of Malaysian crude natural gas, analyzed by using Gas Chromatography-Mass Spectroscopy (GC-MS). It is primarily consists of low density hydrocarbons (methane, ethane, propane) and impurities (CO_2, H_2S, O_2, N_2 etc). Table 1.2 reveals the general chemical composition of crude natural gas from United States.

Table 1.1: Chemical composition of crude natural gas from Telaga Bergading, Petronas Carigali Sdn. Bhd. (Laboratory Services Unit (UNIPEM), 2003).

Gases	Composition (%)
CH_4	47.9
C_2H_6	5.9
C_3H_8	3.2
CO_2	23.5
H_2S	5.4
Others (CO, O_2, N_2)	24.1

Table 1.2: General chemical composition of crude natural gas from United States (Kiricsi and Guczi, 1999).

Gases	Composition (%)
CH_4	89.5
C_2H_6	5.1
C_3H_8	0.7
CO_2	2.5
H_2S	1.0
Others (CO, O_2, N_2)	2.2

Table 1.1 and 1.2 show the purity of Malaysian natural gas is lower than the United State's natural gas. Malaysian crude natural gas is categorized as a sour gas due to the contamination of H_2S. Hydrogen sulfide is the most toxic contaminant in the natural gas. The hydrogen sulfide in natural gas has several possible sources. One is the decomposition of amino acids which contain the thiol functional group, -SH. The anaerobic decay of sulfur-containing proteins or their thermal

decomposition at mild conditions could liberate the sulfur as H_2S. Another potential source is the anaerobic reduction of the sulfate ion, without its first being converted into organic sulfur compounds (Schobert, 1990). This gas is undesirable for several reasons. H_2S itself has an unpleasant smell, being the compound responsible for the unforgettable odour of rotten eggs. H_2S in the presence of water is extremely corrosive and can cause premature failure of valves, pipelines and pressure vessels. It can also cause catalyst poisoning in refinery vessels and necessitates that many other expensive precautionary measures be taken. Besides that, if H_2S is present in the gas when it is burned, sulfur oxides are formed as products of combustion. Not only the sulfur oxides themselves have irritating odors, but they also dissolves in water to form sulfurous and sulfuric acids, which are very corrosive. Most pipeline specifications limit H_2S content to 0.25 grain per 100 cf of gas, equivalent to about four parts per million (Petroleum Extension Service, 1972).

On the other hand, carbon dioxide is considered as diluents, which has no heating value. Therefore, CO_2 might reduce the heating value (Btu/ cf) below acceptable limits. This compound occupies space and is normally a part of the hydrocarbon environment. There are many disadvantages in having diluents in the gas stream, most associated with horsepower, pipeline capacity, internal corrosion, and freezing. The presence of carbon dioxide may enhance the formation of carbonic acid when it reacts with the vapour. Blocks of dry ice may lead to the corrosion and clogging to the process and delivery pipeline.

Typical pipeline-quality natural gas is composed of four main groups of compounds, 90-95% is made up of methane (CH_4); 2-4% is ethane (C_2H_6). Heavier ends through the C_6's constitute 2-3%, 0.5-4% is CO_2 and N_2 as diluents with traces of water vapor and contaminants (Schobert, 1990). Natural gas that contains corrosive elements such as H_2S and CO_2 must be conditioned so that the flow-system equipment does not deteriorate and become a safety hazard or an economic loss. During corrosion of the pipeline, it disintegrates and loses its structural strength. If small quantities are involved, the conditioning may be by the injection of chemical inhibitors into the gas stream; if the quantities are large, the most economical method may be removal of the contaminant or the worst is where a gas pipeline renewal is

needed. Normally pipelines of 32 inches outer diameter or larger are assumed to be onshore projects. Offshore projects are normally involved pipelines with outer diameter of less than 30 inches. According to Oil and Gas Journal's Pipeline Economics Report (Warren, 1999; True, 1999), for proposed U.S. gas pipeline projects in the 1997-98 periods surveyed, the average land cost per mile was more than \$1.2 million/ mile. On the other hand, the off shore projects proposed average more than \$1.5 million/ mile. These figures show how the corrosion of the acidic gases leading to the severe economic loss. Besides, H_2S and CO_2 as the major impurities in Malaysian natural gas also reduce the quality and thus the market price of the gas. Therefore, our country is seeking for an efficient way to increase the production and the quality of our natural gas.

1.3   Current Technologies used in Purification of Natural Gas

Gas purification involves the removal of vapour-phase impurities from gas streams. A variety of conventional separation methods are presently being used to remove the "acid gasses" CO_2 and H_2S from crude natural gas. Some are selective for only H_2S removal, some only for CO_2 removal. However, commercial application of the various gas-purification processes are frequently plagued by unpredictable problems of corrosion (Lieberman, 1987), side reactions, foaming (Cury, 1981), and catalyst deactivation (Trimm, 1980).

Iron-sponge process is the oldest and also the most limited known for removal of sulfur compounds. It is a dry process consisting of iron oxide (Fe_2O_3) impregnated on wood chips or shavings. It is usually used on small gas volumes with low H_2S contents. A vessel can operate 30 to 60 days either without any regeneration or with the partial generation that can be affected with air passage through the vessel. The vessel must be recharged with new iron-sponge material when gas sweetening is no longer possible. This process is selective toward H_2S. If there is CO_2 in the stream, it will not be affected (Petroleum Extension Service, 1972). The primary disadvantage of this process is the difficult change out operation

and disposal of the spent sponge. Hydrogen sulfide can also be removed by stripping. However, a toxic waste stream is created. The waste stream typically contains a high concentration of hydrogen sulfide (H_2S) plus trace amounts of heavy hydrocarbons.

The most widely used process in industry, the alkanolamine process, is a continuous operation liquid process using absorption for the acid gas removal with subsequent heat addition to strip the acid gas components from the absorbent solution. The alkanolamine absorbing solution is not selective and absorbs total acid gas components. The absorbing alkanolamine solution (weak base) chemically reacts with the H_2S and/ or CO_2 (weak acid) to give a water soluble salt. Similarly, a significant amount of waste was formed with the absorption (Petroleum Extension Service, 1972).

Membranes have clear advantage in terms of compactness, not having moving parts and being noise free. The issue not considered in this study is the environment impact of the permeate product streams. These streams will contain substantial amounts of wastes and cannot be discharged to the atmosphere. For this reason and also because of economic consideration the permeate streams will have to be treated by a suitable sulfur recovery process. In addition, the life spans of membranes are limited. They may need to be restored after some time (Hao *et al.*, 2002).

The Shell sulfinol process is unique in that it uses a mixture of solvents, which allows it to behave as both a chemical and physical solvent process. The solvent is composed of sulfolane, DIPA (di-isopropanolamine) and water. The sulfolane acts as the physical solvent while DIPA acts as the chemical solvent. This combination of absorption capabilities offers advantages both for loading and uploading of the solvent. In general, carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptans can be satisfactorily removed from the feed gas, along with H_2S and CO_2, within certain limitations of concentrations in the feed gas. Disadvantages of sulfinol are: (i) the absorption of heavy hydrocarbons and aromatics and (ii) the expensive nature of the sulfolane in the solvent (Petroleum Extension Service, 1972).

Recently, the removal of sour gases via chemical conversion technique using catalyst becomes the most promising technique. Methanation has received attention from a viewpoint of environmental protection because the emission of CO_2 in the atmosphere brings about global warming by the greenhouse effect and these harmful gases can simultaneously be converted to useful methane gas (Hayakawa *et al.*, 1999). This process can increase the purity of the natural gas without wasting the undesired components but fully used them to increase the concentration of methane. However, this reaction is an eight electron process involving thermodynamics. It is difficult to achieve this reaction under mild conditions due to kinetic barriers. These conditions are inconvenient in a laboratory because they required specialized equipment, and the rate of the reaction is difficult to control. Therefore, the development of catalysts to lower the activation energy of this reaction is needed.

On the other hand, hydrogen sulfide in the crude natural gas can be reduced to elemental sulfur by the Claus process. H_2S is partially burned to create a mixture of H_2S and sulfur dioxide (SO_2). The H_2S and SO_2 then react in the presence of a catalyst to form sulfur and water. Sulfates formation is an undesired side reaction of Claus catalyst. However, when the proper metals are used, the spinel compound from the catalyst reacts to form sulfates that are unstable enough to react with H_2S and other compounds to form elemental sulfur. Thus, sulfates do not inhibit catalyst performance. Then the sulfur produced can be sold commercially. There are problem arises when significant amounts of hydrocarbons reduce the catalyst efficiency. Hydrocarbons reduce to form graphite, which contaminates the sulfur.

Equation 1.1 shows the general H_2S desulfurization reaction while Equation 1.2 shows the stoichiometric equation for CO_2/ H_2 conversion to methane or higher hydrocarbons.

$$H_2S_{(g)} + \tfrac{1}{2} O_{2\,(g)} \quad \rightarrow \quad S_{(s)} + H_2O_{(l)} \qquad \text{(Equation 1.1)}$$

$$CO_{2\,(g)} + 4H_{2\,(g)} \rightarrow CH_{4\,(g)} + C_2H_{6\,(g)} + C_3H_{8\,(g)} \ldots + \; 2H_2O_{(l)} \quad \text{(Equation 1.2)}$$
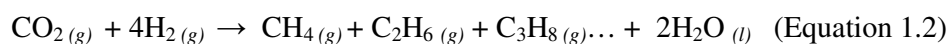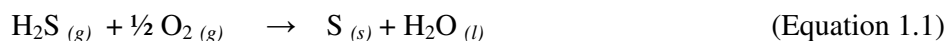
Besides that, co-generation of heat is also possible because the methanation of CO_2 is an exothermic reaction, with ΔH = -165 kJ/mol. Removal of H_2S is an oxidation reaction, while removal of CO_2 is a reduction reaction. Enthalpies of the reduction and oxidation reactions play an important role. CO_2 in this case can act as an oxidizing agent.

$$H_2S_{(g)} + CO_{2\,(g)} \rightarrow SO_{2\,(g)} + 2CO_{(g)} + H_{2\,(g)} \quad\quad\quad \text{(Equation 1.3)}$$
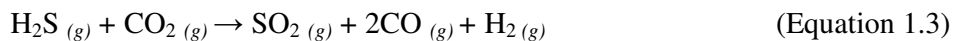
The CO produced in the previous step can be converted to CH_4 in the presence of H_2, as shown in Equation 1.4.

$$CO_{(g)} + 3H_{2\,(g)} \rightarrow CH_{4\,(g)} + H_2O_{(l)} \quad\quad\quad \text{(Equation 1.4)}$$

Catalytic activity is defined as the rate at which a chemical reaction reaches the equilibrium. From the industrial point of view, activity is also defined as the amount of reactant transformed into product per unit of time and unit of reactor volume. Meanwhile, the selectivity of a catalyst is defined as the rate of reactant conversion into the desired products. Selectivity usually depends on reaction parameters such as temperature, pressure, reactants composition and also on the catalyst nature. Therefore, the main effect of a catalyst is to provide an alternative reaction path that permits to decrease the activation energies of the different reaction steps, reaching therefore the equilibrium in an easier and faster way. On the other hand, the catalyst should be high selectivity towards yielding of CH_4 and minimizes the possibility of side reactions. Equation 1.5 shows an undesired side reaction in this study.

$$CO_{2\,(g)} + H_{2\,(g)} \rightarrow CO_{(g)} + H_2O_{(l)} \quad\quad\quad \text{(Equation 1.5)}$$

1.4   Objectives of the Research

The ultimate goal of this research is to synthesize a novel catalyst that is able to catalyze the in-situ reactions of CO_2/ H_2 methanation and H_2S desulfurization at a very low temperature with 100 % conversion.

The objectives of this research are:

- To synthesize and modify supported Ni based catalyst for the in-situ reactions of methanation and desulfurization;

- To elucidate the catalytic activity of the prepared catalysts;

- To characterize and propose the active site of an excellent catalyst.

1.5   Scope of the Research

Various supported catalysts were prepared to catalyze the in-situ reactions of CO_2/ H_2 methanation and H_2S desulfurization. In this research, dopants were chosen from the first row transition metal and rare earth metal to be added towards nickel oxide based catalyst. First, study on different ratio of the metal oxides to nickel was carried out. Then, different possible supports were tried on the potential catalysts to propose the best support. The catalytic activities of the prepared catalysts were tested using a home-built microreactor coupled with Fourier Transform Infrared Spectroscopy. The production of methane gas was detected by Gas Chromatography analysis to determine the yielding of methane. All the studies will be done based on trial and error method where different mixed metal oxides with different ratio were tested until the best performance catalyst was obtained. The characteristics of the novel catalyst were confirmed by the use of X-ray Photoelectron Spectroscopy for active surface components, X-Ray Diffraction for bulk structure, Field Emission Scanning Electron Microscope for morphology study, Energy Dispersive X-Ray Analysis for elemental composition study, Nitrogen Adsorption for pore texture and surface area of the catalyst, Fourier Transform Infrared Spectroscopy for the functional group study and Thermogravimetry Analysis to study the mass loss of the catalyst during temperature change. The active sites of the novel catalyst would be

proposed. In general, it is a very demanding task to make a useful comparison of activity and selectivity of a catalyst under conditions appropriate for commercial operation.

References

Agnelli, M. and Mirodatos, C. (2000). CO hydrogenation on nickel-based catalysts: Effects of copper addition. *Journal of Catalysis.* 192, 204-214. Elsevier.

Akanuma, K., Nishizawa, K., Kadama, T., Mimora, K., Yoshida, T., Tsuji, M. and Tamaura, Y. (1993). Carbon dioxide decomposition into carbon with the rhodium-bearing magnetite activated by H_2-reduction. *Journal of Materials Science.* 28, 860-864. Springer.

Arnoldy, P. and Moulijn, J.A. (1985). Temperature-programmed reduction of CoO/ Al_2O_3 catalysts. *Journal of Catalysis.* 93, 38-54.

Barcicki, J., Borowiecki, T., Grzegorczyk, W., Nazimek, D., Denis, A. and Pielach, M. (1981). Effect of hydrogen sulfide on the activity of nickel catalysts for methanation. *Reaction Kinetics and Catalysis Letters.* 18 (3-4), 437-442.

Barr, T.L. (1981). An ESCA study of the termination of passivation of elemental metals. *The Journal of Physical Chemistry.* 82 (16), 1801-1810.

Bartholomew, C. H., Weatherbee, G. D. and Jarvi, G. A. (1979). Sulfur poisoning of nickel methanation catalysts I. In-situ deactivation by H_2S of nickel and nickel bimetallics. *Journal of Catalysis.* 60(2), 257-269.

Bartholomew, C. H. and Uken, A. H. (1982). Metal boride catalysts in methanation of carbon monoxide III. Sulfur resistance of nickel boride catalysts compared to nickel and raney nickel. *Applied Catalysis.* 4, 19-29.

Blanchard, F., Reymond, J.P., Pommier, B. and Teichner, S.J. (1982). On the mechanism of the Fischer-Tropsch synthesis involving unreduced iron catalyst. *Journal of Molecular Catalysis.* 17, 171-181.

Burch, R. and Flambard, A.R. (1984). Support effects in nickel catalysts. *Journal of Catalysis.* 85, 16-24.

Carpentier, J., Siffert, S., Lamonier, J.F., Laversin, H. and Aboukaïs. (2007). Synthesis and characterization of Cu-Co-Fe hydrotalcites and their calcined products. *Journal of Porous Materials.* 14, 103-110. Springer.

Castaño, P., Pawelec, B., Fierro, J.L.G., Arandes, J.M. and Bilbao, J. (2007). Enhancement of pyrolysis gasoline hydrogenation over Pd-promoted Ni/ SiO_2– Al_2O_3 catalysts. *Fuel.* 86, 2262-2274. Elsevier.

Cerro-Alarcón, M., Bachiller-Baeza, B., Guerrero-Ruiz, A. and Rodríguez-Ramos, I. (2006). Effect of the reduction–preparation method on the surface states and catalytic properties of supported-nickel particles. *Journal of Molecular Catalysis A: Chemical.* 258, 221-230. Elsevier.

Chang, F.W., Kuo, M.S., Tsay, M.T. and Hsieh, M.C. (2003). Hydrogenation of CO_2 over nickel catalysts on rice husk ash-alumina prepared by incipient wetness impregnation. *Applied catalysis A: General.* 247, 309-320. Elsevier.

Cury, R.N. (1981). *Fundamentals of Natural Gas Conditioning.* Tulsa, Oklahoma: Penn Well Publishing Company.

Curtis, V., Nicolaides, C.P., Coville, N.J., Hildebrandt, D. and Gilasser, D. (1999). The effect of sulfur on supported cobalt Fischer-Tropsch catalysts. *Catalysis Today.* 49, 33-40. Elsevier.

Czekaj, I., Loviat, F., Raimondi, F., Wambach, J., Biollaz, S. and Wokaun, A. (2007). Characterization of surface processes at the Ni-based catalyst during the metantaion of biomass-derived synthesis gas: X-ray Photoelectron Spectroscopy (XPS). *Applied Catalysis A: General.* 329, 68-78. Elsevier.

Davis, B.H. (2007). Fischer-Tropsch Synthesis: Comparison of performances of iron and cobalt catalysts. *Industrial and Engineering Chemistry Research.* 46, 8938-8945. American Chemical Society.

De Boer, M., van Dillen, A.J., Koningsberger, D.C., Geus, J., Vuurman, M.A. and Wachs, I.E. (1991). Remarkable spreading behavior of molybdena on silica catalysts. An *in situ* EXAFS-Raman study. *Catalysis Letter.* 11, 227-240. Springer.

Deo, G. and Wachs, I.E. (1991). Predicting molecular structures of surface metal oxide species on oxide supports under ambient conditions. *The Journal of Physical Chemistry.* 95, 5889-5895.

Djaidja, A., Barama, A. and Bettahar, M.M. (2000). Oxidative transformation of methane over nickel catalysts supported on rare-earth metal oxides. *Catalysis Today.* 61, 303-307. Elsevier.

Dong, X.L., Zhang, Z.D., Jin, S.R., Sun, W.M. and Chuang, Y.C. (1998). Surface characterizations of ultrafine Ni particles. *Nano Structured Materials.* 10 (4), 585-592. Pergamon.

El-Shobaky, G.A., El-Molla, S.A. and Ali, A.M.I. (2003). Catalytic promotion of NiO/MgO system by doping with some transition metal cations. *Applied Catalysis A: General.* 253, 417-425. Elsevier.

Erhan Aksoylu A. and İlsen Önsan, Z. (1997). Hydrogenation of carbon dioxides using coprecipitated and impregnated Ni/Al_2O_3 catalysts. *Applied Catalysis A: General.* 164, 1-11. Elsevier.

Erhan Aksoylu, A., İnci İsli, A. and İlsen Önsan, Z. (1999). Interaction between nickel and molybdenum in $Ni-Mo/Al_2O_3$ catalysts: III. Effect of impregnation strategy. *Applied Catalysis A: General.* 183, 357-364. Elsevier.

Fadley, C.S. and Shirley, D.A. (1969). Multiplet splitting of core-electron binding energies in transition metal ions. *Physical Review Letters.* 23 (24), 1397-1401.

Finch, J. N. (1979). United States Patent 4168276. Retrieved on September 18, 1979 from http://patft.uspto.gov/

Finch, J.N. and Ripley, D.L. (1976). United States Patent 3988334. Retrieved on October 26, 1976 from http://www.freepatentsonline.com/

Fournier, J. A. (1986). *Characterization of some iron catalysts for the reduction of carbon monoxide and the effect of residence time and temperature on the nature of carbon monoxide reduction products.* PhD Thesis. Brown University, United States of America.

Galtayries, A. and Grimblot, J. (1999). Formation and electronic properties of oxide and sulphide films of Co, Ni and Mo studied by XPS. *Journal of Electron Spectroscopy and Related Phenomena.* 98–99, 267–275. Elsevier.

Garcia, L., French, R., Czernik, S. and Chornet, E. (2000). Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Applied Catalysis A: General.* 201, 225-239. Elsevier.

Hao, J., Rice, P.A. and Stern, S.A. (2002). Upgrading low-quality natural gas with H_2S- and CO_2-selective polymer membranes Part I-Process design and economics of membranes stages without recycle streams. *Journal of Membrane Science.* 209, 177-206. Elsevier.

Happel, J. and Hnatow, M. A. (1981). United States Patent 4260553. Retrieved on April 7, 1981 from http://patft.uspto.gov/

Han, Y.S., Li, J.B., Ning, X.S., Yang, X.Z. and Chi, B. (2004). Study on NiO excess in preparing NiAl$_2$O$_4$. *Materials Science and Engineering A.* 369, 241-244. Elsevier.

Hashimoto, K., Yamasaki, M., Meguro, S., Sasaki, T., Katagiri, H., Izumiya, K., Kumagai, N., Habazaki, H., Akiyama, E. and Asami, K. (2002). Materials for global carbon dioxide recycling. *Corrosion Science.* 44, 371-386. Elsevier.

Hayakawa, T., Suzuki, S., Nakamura, J., Uchijima, T., Hamakawa, S., Suzuki, K., Shishido, T. and Takehira, K. (1999). CO$_2$ reforming of CH$_4$ over Ni/ perovskite catalysts prepared by solid phase crystallization method. *Applied Catalysis A: General.* 183, 271-285. Elsevier.

Iamir, E. M., Aliwi, S. M. and Naman, S. A. (2006). Thermal reduction of CO$_2$ in the presence of H$_2$S. *Petroleum Science and Technology.* 24, 117-127. Taylor and Francis.

Iglesia, E. (1997). Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. *Applied Catalysis A: General.* 161, 59-78. Elsevier.

Inui, T., Funabiki, M., Suehiro, M. And Sezume, T. (1979). Methanation of CO$_2$ and CO on supported nickel-based composite catalysts. *Journal of the Chemical Society, Faraday Transaction.* 75, 787-802.

Inui, T. (1996). Highly effective conversion of carbon dioxide to valuable compounds on composite catalysts. *Catalysis Today.* 29, 329-337. Elsevier.

Iyer, M., Ramkumar, S. and Fan, L.S. (2006). Enhanced hydrogen production integrated with CO$_2$ separation in a single type of report. *Annual Technical Progress Report.* United States of America: The Ohio-State University.

Jackson, S.D. and Wells, P.B. (1986). Metal clusters as catalyst sites: Site-support and site-carbon interactions. *Applied Catalysis.* 25, 157-163.

Jaggi, N. and Vij, D.R. (2006). Fourier Transform Infrared Spectroscopy. In Vij, D.R. (Ed.) *Handbook of Applied Solid State Spectroscopy.* (pp. 411-450). New York, USA: Springer. Ming, Jiang, Naoto Koizumi and Muneyoshi Yamada. Adsorption properties of Iron and Iron-Manganese Catalysts investigated by in-situ Diffuse Reflectance FTIR spectroscopy. *Journal of Physical Chemistry B.* 2000. 104: 7636-7643.

Jiang, M., Koizumi, N. and Yamada, M. (2000). Adsorption properties of Iron and Iron-Manganese Catalysts investigated by in-situ Diffuse Reflectance FTIR spectroscopy. *The Journal of Physical Chemistry B.* 104, 7636-7643. American Chemical Society.

Jiang, X.Z., Stevenson, S.A., Dumesic, J. A., Thomas F. Kelly, T.F. and Casper, R.J. (1984). Characterization of NiFe Alloy Particles Supported on Titania and Alumina: Scanning Transmission Electron Microscopy, Magnetic Susceptibility, Mossbauer Spectroscopy, and Chemisorption Measurements. *The Journal of Physical Chemistry.* 88, 6191-6198.

Jose, A., R., Jonathan, C., H., Anatoly, I., F., Jae, Y., K. and Manuel, P. (2001). Experimental and theoretical studies on the reaction of H_2 with NiO. Role of O vacancies and mechanism for oxide reduction. *Journal of the American Chemical Society.* 124, 346-354. America Chemical Society.

Kherbeche, A., Benharref, A. and Hubaut, R. (1996). Sulfur poisoning of nickel-rare-earth based catalysts. *Reaction Kinetics and Catalysis Letters.* 57 (1), 13-20. Springer.

Kiennemann, A., Kieffer, R. and Chornet, E. (1981). CO/ H_2 and CO_2/ H_2 reactions with amorphous carbon-metal catalysts. *Reaction Kinetics and Catalysis Letters.* 16 (4), 371-376. Springer.

Kim, K.S. (1975). X-ray photoelectron spectroscopic studies of the electronic structure of CoO. *Physical Review B.* 11 (6), 2177-2187.

Kiricsi, I. and Guczi, L. (1999). Environmental Friendly Reactions and Technologies. *Applied Catalysis.* 189, 151-276. Elsevier.

Kodama, T., Kitayama, Y., Tsuji, M. and Tamaura, Y. (1997). Methanation of CO_2 using ultrafine $Ni_xFe_{3-x}O_4$. *Energy.* 22 (2-3), 183-187. Elsevier.

Kohl, A.L. and Riesenfeld, F.C. (1985). *Gas Purification.* 4th. ed. United States of America: Gulf Publishing Company.

Kozhukharov, V., Machkova, M. and Brashkova, N. (2003). Sol-gel route and characterization of supported perovskites for membrane applications. *Journal of Sol-Gel Science and Technology.* 26, 753-757. Springer.

Krylov, O.V., Mamedov, A.Kh. and Mirzabekova, S.R. (1998). Interaction of carbon dioxide with methane on oxide catalysts. *Catalysis Today.* 42, 211-215. Elsevier.

Kulshreshtha, S. K., Sasikala, R., Gupta, N. M. and Iyer, R. M. (1990). Carbon monoxide methanation over $FeTi_{1-x}Sn_x$ intermetallics: Role of second phase. *Catalysis Letter.* 4 (2), 129-138. Springer.

Kunz, U., Kirschning, A., Wen, H.L., Solodenko, W., Cecilia, R., Kappe, C.O. and Turek, T. (2005). Monolith polymer/ carrier mmaterials: Versatile composites for fine chemical synthesis. *Catalysis Today.* 105, 318-324. Elsevier.

Laboratory Services Unit, UNIPEM. (2003). Faculty of Chemical Engineering and Natural Resources Engineering, Universiti Teknologi Malaysia. 49-52.

Lamber, R. and Schulz-Ekloff, G. (1991). Characterization of microstructures in nickel alumina catalysts by analytical electron microscopy. *Surface Science.* 258 (1-3), 107-118.

Li, G.H., Hu, L.J. and Hill, J.M. (2006). Comparison of reducibility and stability of alumina-supported Ni catalysts prepared by impregnation and co-precipitation. *Applied Catalysis A: General.* 301, 16-24. Elsevier.

Li, T.Z., Yang, Y., Zhang, C.H., Tao, Z.C., Wan, H.J., An, X., Xiang, H.W. and Li, Y.W. (2007). Effect of Manganese incorporated manner on an iron-based catalyst for Fischer-Tropsch synthesis. *Journal of Natural Gas Chemistry.* 16, 244-251. Elsevier.

Li, Y.M., Wang, R.J. and Chang, L. (1999). Study of reactions over sulfide catalysts in $CO-CO_2-H_2-H_2O$ system. *Catalysis Today.* 51: 25-38. Elsevier.

Lieberman, N.P. (1987). *Troubleshooting Natural Gas Processing-Wellhead to Transmission.* Tulsa, Oklahoma: Penn Well Publishing Company.

Lorenz, P., Finster, J., Wendt, G., Salyn, J.V., Žumadilov, E.K. and Nefedov, V.I. (1979). ESCA investigations of some NiO/ SiO_2 and $NiO-Al_2O_3/ SiO_2$ catalysts. *Journal of Electron Spectroscopy and Related Phenomena.* 16, 267-276.

Macêdo, M.I.F., Bertran, C.A. and Osawa, C.C. (2007). Kinetics of the $\gamma \rightarrow \alpha$ alumina phase transformation by quantitative X-ray diffraction. *Journal of Material Science.* 42, 2830-2836. Springer.

Malaysia Oil and Gas, 2007

http://www.yellowpages.com.my/energyguide/

Martínez, R., Romero, E., Guimon, C. and Bilbao, R. (2004). CO_2 reforming of methane over coprecipated Ni–Al catalysts modified with lanthanum. *Applied Catalysis A: General.* 274, 139-149. Elsevier.

Mashapa, T.N., Rademan, J.D. and Vuuren, J.J. (2007). Catalytic performance and deactivation of precipitated iron catalyst for selective oxidation of hydrogen sulfide to elemental sulfur in the waste gas streams form coal gasification. *Industrial and Engineering Chemistry Research.* 46, 6338-6344. American Chemical Society.

McIntyre, N.S. and Zetaruk, D.G. (1977). X-ray photoelectron spectroscopic studies of iron oxides. *Analytical Chemistry.* 49 (11), 1521-1529.

Medina, J.C., Butala, S.J., Bartholomew, C.H. and Lee, M.L. (2000a). Iron-catalyzed CO_2 hydrogenation as a mechanism for coalbed gas formation. *Fuel.* 79, 89-93. Elsevier.

Medina, J.C., Butala, S.J., Bartholomew, C.H. and Lee, M.L. (2000b). Low temperature iron- and nickel-catalyzed reactions leading to coalbed gas formation. *Geochimica et Cosmochimica Acta.* 64 (4), 643-649. Pergamon.

Md. Yassin, A.A. (1987). Natural-gas future energy for Malaysia. *Third Symposium of Malaysian Chemical Engineers.* 15-16 June. Kuala Lumpur, Malaysia: Universiti Teknologi Malaysia, 1-3.

Miao, Q., Xiong, G., Sheng, S., Cui, W., Xu, L. and Guo, X. (1997). Partial oxidation of methane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide. *Applied Catalysis A: General.* 154, 17-24. Elsevier.

Mori, S., Xu, W. C., Ishidzuku, T., Ogasawara, N., Imai, J. and Kobayashi, K. (1998). Mechanochemical Activation of Catalysts for CO2 Methanation. *Applied Catalysis A: General.* 137, 255-268. Elsevier.

Moulder, J.F., Stickle, W.F., Sobol, P.E. and Bomben, K.D. (1992). *Handbook of X-ray Photoelectron Spectroscopy.* United States of America: Perkin-Elmer Corporation.

Mueller, J. (2004a). Natural gas vs coal in Asian power struggle. *Asian Oil & Gas,* March/ April 2004, 14-15.

Mueller, J. (2004b). Surging demand energies Asian investment plans. *Asian Oil & Gas,* January/ February 2004, 14-16.

Nascente, P.A.P. (2005). Materials characterization by X-ray photoelectron spectroscopy. *Journal of Molecular Catalysis A: Chemical.* 228, 145-150. Elsevier.

Natile, M.M. and Glisenti, A. (2003). New NiO/ Co_3O_4 and Fe_2O_3/ Co_3O_4 nanocomposite catalysts: Synthesis and characterization. *Chemistry of Materials.* 15, 2502-2510. American Chemical Society.

Naumann, A. W. and Behan, A. S. (1979). *U.S. Patent 4243554.* Retrieved on January 6, 1981, from http://www.uspto.gov/patft/

Nefedov, V.I., Gati, D., Dzhurinskii, B.F., Sergushin, N.P. and Salyn, Ya.V. (1975). Simple and coordination compounds. *Russian Journal of Inorganic Chemistry.* 20, 2307-2314.

Niemantsverdriet, J. W. (1993). *Spectroscopy in Catalysis: An Introduction.* Federal Republic of Germany: VCH Verlagsgesellschaft mbH.

Nikolova, D., Edreva-Kardjieva, R., Gouliev, G., Grozeva, T. and Tzvetkov, P. (2006). The state of (K)(Ni)Mo/g-Al2O3 catalysts after water–gas shift reaction in the presence of sulfur in the feed: XPS and EPR study. *Applied Catalysis A: General.* 297, 135-144. Elsevier.

Olah, G. A. and Molnár, Á. (2003). *Hydrocarbon Chemistry.* 2nd. ed. New Jersey, USA: John Wiley & Sons, Inc.

Petroleum Extension Service. (1972). *Field Handling of Natural Gas.* (3rd ed.) The University of Texas at Austin: Petroleum Extension Council.

Reguig, B.A., Regragui, M., Morsli, M., Khelil, A., Addou, M. and Bernède, J.C. (2006). Effect of the precursor solution concentration on the NiO thin filmproperties deposited by spray pyrolysis. *Solar Energy Materials and Solar Cells.* 90, 1381-1392. Elsevier.

Rethwisch, D.G. and Dumesic, J.A. (1988). Adsorptive and catalytic properties of carbon monoxide and carbon dioxide over supported metal oxides. In Ayers, W.T. (Ed.) *Catalytic activation of Carbon Dioxide.* (pp. 102-122). Washington, DC: American Chemical Society.

Richardson, J.T. and Twigg, M.V. (1998). Reduction of impregnated NiO/ α-Al$_2$O$_3$. Association of Al^{3+} ions with NiO. *Applied Catalysis A: General.* 167, 57-64. Elsevier.

Riedel, T. and Schaub, G. (2003). Low-temperature Fischer-Tropsch synthesis on cobalt catalysts – effects of CO_2. *Topics in Catalysis.* 26: 145-156. Springer.

Saito, M. and Anderson, R.B. (1981). The activity of several molybdenum compounds for the methanation of CO_2. *Journal of Catalysis.* 67, 296-302.

Salagre, P., Fierro, J.L.G., Medina, F. and Sueiras, J.E. (1996). Characterization of nickel species on several γ-alumina supported nickel samples. *Journal of Molecular Catalysis A: Chemical.* 106, 125-134. Elsevier.

Savva, P.G., Goundani, K., Vakros, J., Bourikas, K., Fountzoula, Ch., Vattis, D., Lycourghiotis, A. and Kordulis, Ch. (2008). Benzene hydrogenation over Ni/ Al_2O_3 catalysts prepared by conventional and sol-gel techniques. *Applied Catalysis B: Environmental.* 79, 199-207. Elsevier.

Schneeman, J.G. (1968). *Industrial X-ray Interpretation.* United States of America: Intex Publishing Company.

Schobert, H. H. (1990). *The Chemistry of Hydrocarbon Fuels.* England: Butterworth & Co (Pulishers) Ltd.

Seemann, M.C., Schildhaver, T.J., Biollaz, S.M.A., Stucki, S. and Wokaun, A. (2006). The regenerative effect of catalyst fluidization under methanation conditions. *Applied Catalysis A: General.* 313, 14-21. Elsevier.

Shields, M.A., Dowling, N.I. and Clark, P.D. (2007). Catalytic H_2S conversion and SO_2 production over iron oxide and iron oxide/ $γ-Al_2O_3$ in liquid sulfur. *Industrial & Engineering Chemistry Research.* 46, 7721-7728. American Chemical Society.

Sikorska-Iwan, M., Mrozek, R., Ostasz, A. and Rzaczynska, Z. (2003). Thermal Investigations Of Dehydration Of Lanthanide(III) 5-Nitroanthranilates. *Journal of Thermal Analysis and Calorimetry.* 74, 529-536.

Silver, R.G., Jackson, N.B. and Ekerdt, J.G. (1988). Adsorption and reaction of carbon dioxide on zirconium dioxide. In Ayers, W.T. (Ed.). *Catalytic activation of Carbon Dioxide.* (pp. 123-132). Washington, DC: American Chemical Society.

Smet, F.D., Ruiz, P., Delmon, B. and Devillers, M. (1996). Catalytic behaviour of multiphasic oxide catalysts containing lanthanides (La, Ce, Pr, Sm, Tb) in the selective oxidation of isobutene to methacrolein. *Catalysis Letters.* 41, 203-207. Springer.

Somorjai, G.A. (1972). On the mechanism of sulphur poisoning of platinum catalysts. *Journal of Catalysis.* 27, 453-456.

Somorjai, G.A. (1994). *Introduction to the Surface Chemistry and Catalysis.* New York, United States of America: John Wiley & Sons, Inc.

Song, Z., Bao, X., Wild, U., Muhler, M. and Ertl, G. (1998). Oxidation of amorphous Ni-Zr alloys studied by XPS, UPS, ISS and XRD. *Applied Surface Science.* 134, 31-38. Elsevier.

Souma, Y., Ando, H., Fujiwara, M. and Kieffer, R. (1995). Catalytic hydrogenation of carbon dioxide to hydrocarbons. *Energy Conversion and Management.* 36 (6-9), 593-596. Elsevier.

Spencer, M.J.S. and Yarovsky, I. (2007). Ab-Initio molecular dynamics study of H_2S dissociation on the Fe(110) surface. *The Journal of Physical Chemistry C.* 111, 16372-16378. American Chemical Society.

Stoop, F., Verbiest, A.M.G. and Van Der Wiele, K. (1986). The influence of the support on the catalytic properties of Ru catalysts in the CO hydrogenation. *Applied Catalysis.* 25, 51-57.

Su, B.L. and Guo, S.D. (1999). Effects of rare earth oxides on stability of $Ni/\alpha-Al_2O_3$ catalysts for steam reforming of methane. *Studies in Surface Science and Catalysis.* 126, 325-332.

Takenaka, S., Shimizu, T. and Otsuka, K. (2004). Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts. *International Journal of Hydrogen Energy.* 29, 1065-1073. Elsevier.

Tanabe, K. and Yamaguchi, T. (1994). Acid-base bifunctional catalysis by ZrO_2 and its mixed oxides. *Catalysis Today.* 20 (2), 185-197.

Tavares, M. T., Alstrup, I., Bernardo, C. A. and Rostrup-Nielsen, J. R. (1996). Carbon formation and CO methanation on silica-supported nickel and nickel-copper catalystsin $CO + H_2$ mixtures. *Journal of Catalysis.* 158, 402-410.

Trimm, D. L. (1980). *Design of Industrial Catalyst.* The Netherlands: Elsevier Scientific Publishing Company.

True, W. R. W. (1999). Construction inflation could squeeze North American pipelines. *Oil & Gas Journal.* 96 (35), 33-55.

Tsuji, M., Kato, H., Kodama, T., Chang, Shih Ger, Hesegawa, N. and Tamaura, Y. (1994). Methanation of CO_2 on H_2-reduced Ni (II)- or Co (II)-bearing ferrites at 200 ^{o}C. *Journal of Materials Science.* 29, 6227-6230.

Vannice, M. A. J. (1977). The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the Group VIII metals V. The catalytic behavior of silica-supported metals. *Journal of Catalysis.* 50(2), 228-236.

Vannice, M.A. and Garten, R.L. (1979). Metal-support effects on the activity and selectivity of Ni catalysts in CO/H_2 synthesis reactions. *Journal of Catalysis.* 56 (2), 236-248.

Vederine, J.C., Hollinger, G. and Minh, O.T. (1978). Investigations of Antigorite and Nickel Supported Catalysts by X-ray Photoelectron Spectroscopy. *The Journal of Physical Chemistry.* 82, 1515.

Wachs, I.E. (1996). Raman and IR studies of surface metal oxide species on oxide supports: Supported metal oxide catalysts. *Catalysis Today.* 27, 437-455. Elsevier.

Wachs, I.E. (2005). Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials. *Catalysis Today.* 100, 79-94. Elsevier.

Wambach, J. and Freud, H. (1994). CO_2 activation on transition metal surfaces. In. Paul, J. and Pradier, C.M. (Ed.) *Carbon Dioxide Chemistry: Environmental Issues.* (pp. 31-43). Cambridge, UK: The Royal Society of Chemistry.

Wan Abu Bakar, W.A. (2005). *Personnel Communications.* Universiti Teknologi Malaysia, Skudai.

Wan Abu Bakar, W.A. (2006). *Personnel Communications.* Universiti Teknologi Malaysia, Skudai.

Wan Abu Bakar, W.A. (2007). *Personnel Communications.* Universiti Teknologi Malaysia, Skudai.

Wang, H.T., Xiao, T.C., Su, J.X., Liu, W.X. and Lu, Y.L. (1999). Catalytic purification of flue gas from civil-used stove. *Catalysis Today.* 53, 661-667. Elsevier.

Wang, S.H., Liao, X.Y., Cao, D.B., Huo, C.F., Li, Y.W., Wang, J.G. and Jiao, H.J. (2007). Factors controlling the interaction of CO_2 with transition metal surfaces. *Journal of Physical Chemistry C.* 111, 16934-16940. American Chemical Society.

Wang, W.D., Lin, P.Y., Fu, Y.L. and Cao, G.Y. (2002). Redox properties and catalytic behavior of praseodymium-modified (Ce-Zr)O_2 solid solutions in three- way catalysts. *Catalysis Letters.* 82, 19-27. Springer.

Wang, W.J., Li, H.L., Kang, G.H., Huang, J.Z. and Xu, Z. (2006). Detailed analysis of factors to influence the electrochemical behaviors of Fe: NiOx films fabricated by magnetron sputtering technology. *International Journal of Hydrogen Energy.* 31, 1791 – 1796. Elsevier.

Warren, R. (1999). Pipeline economic uncertainly trims plans for pipeline construction. *Oil and Gas Journal.* 97 (6), 36-41.

Weast, R.C. and Selby, S.M. (Eds.) (1966). *Handbook of Chemistry and Physics.* (47th ed.) Ohio: The Chemical Rubber Co.

Wojcieszak, R., Monteverdi, S., Mercy, M., Nowak, I., Ziolek, M. and Bettahar, M.M. (2004). Nickel containing MCM-41 and AlMCM-41 mesoporous molecular sieves. Characteristics and activity in the hydrogenation of benzene. *Applied Catalysis A: General.* 268, 241-253. Elsevier.

Yamasaki, M., Komori, M., Akiyama, E., Habazaki, H., Kawashima, A., Asami, K. and Hashimoto, K. (1999). CO_2 methanation catalysts prepared from amorphous Ni-Zr-Sm and Ni-Zr-misch metal alloy precursors. *Materials Science and Engineering A.* 267, 220-226. Elsevier.

Yamashita, T. and Hayes, P. (2007). Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials. *Applied Surface Science.* doi: 10.1016/j.apsusc.2007.09.063.

Yan, J.Y., Kung, M.C., Sachtler, W.M.H. and Kung, H.H. (1997). Co/ Al_2O_3 lean NO_x reduction catalyst. *Journal of Catalysis.* 172, 178-186. Elsevier.

Yoon, W.S., Hanson, J., McBreen, J. and Yang, X.Q. (2006). A study on the newly observed intermediates structures during the thermal decomposition of nickel-based layered cathode materials using time-resolved XRD. *Electrochemistry Communications.* 8, 859-862. Elsevier.

Zeng, H.C., Lin, J. and Tau, K.L. (1995). Memory effect of ZrO_2 matrix on surface Co_3O_4-CO position. *Journal of Material Research.* 10, 3096-3105.

Zhang, Y.Q., Jacobs, G., Sparks, D.E., Dry, M.E. and Davis, B.H. (2002). CO and CO_2 hydrogenation study on supported cobalt Fisher-Tropsch synthesis catalysts. *Catalysis Today.* 71, 411-418. Elsevier.

Zhao, N., Xu, R., Wei, W. And Sun, Y.H. (2002). Cu/ Mn/ ZrO_2 catalyst for alcohol synthesis by Fischer-Tropsch modified elements. *Reaction Kinetics and Catalysis Letters.* 75 (2), 297-304. Akadémiai Kiadó, Budapest.

Zheng, H.Y., An, M.Z. and Lu, J.F. (2008). Surface characterization of the Zn-Al-Al$_2$O$_3$ nanocomposite coating fabricated under ultrasound condition. *Applied Surface Science.* 254, 1644-1650. Elsevier.

Zhou, Y., Gu, D.H., Geng, Y.Y. and Gan, F.X. (2006). Thermal, structural and optical properties of NiO$_x$ films deposited by reactive dc-magnetron sputtering. *Materials Science and Engineering B.* 135, 125-128. Elsevier.