INVESTIGATION OF CO HYDROGENATION CATALYSTS FOR PRODUCING OXYGENATED HYDROCARBONS

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ABSTRACT

INVESTIGATION OF CO HYDROGENATION CATALYSTS FOR PRODUCING OXYGENATED HYDROCARBONS

The objective of this study was to test the performance of promoted rhodium catalysts supported on silica for oxygenated hydrocarbon (particularly ethanol) production by CO hydrogenation. Two different catalysts were prepared by incipient wetness impregnation: 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2. Activity tests included a parametric study of the effects of reaction temperature, pressure, contact time (W/F_{CO}) on CO conversion as well as on the selectivity for methane, ethanol and carbon dioxide. The microstructures of catalyst surfaces were characterized by ESEM with EDX analysis. The reaction system consisted of a fixed bed micro-reactor integrated within a fully automated high-pressure reactor system equipped with a programmable logic controller and software for the remote control of the system. Two on-line gas chromatographs (GC and GC-MS) were used for feed and product analysis. Experiments were first conducted on 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 using a fixed inlet composition of 10 mol% CO and 20 mol% H_2 with balance N_2 at a W/F_{CO} ratio of 0.98 mg.min.μmol^{-1}. Reaction conditions were varied in a range of 14-35 bar and 240-315°C. Subsequent experiments were performed at 25 bar and 285°C using W/F_{CO} ratios of 0.49-1.95 mg.min.μmol^{-1} over doubly-promoted Rh/SiO_2. Experiments for singly-promoted catalyst were performed at 270-300°C in the same pressure range at a W/F_{CO} ratio of 0.98 mg.min.μmol^{-1}. Increasing contact times, increasing reaction temperatures and addition of V as a promoter all improved catalytic activity in terms of CO conversion significantly. No significant amount of oxygenated hydrocarbon was produced over Rh-La/SiO_2 whereas ethanol, acetic acid and ethyl ether were detected as major oxygenated products over the doubly promoted Rh-La-V/SiO_2 catalyst. Higher pressures enhanced the formation of oxygenated products. Regarding ethanol selectivity, the highest value obtained was ca. 19% at a CO conversion of 9% (270°C, 35 bar), followed by a selectivity of 15% at 31% CO conversion (300°C, 35 bar). The activity of the catalyst was mostly controlled by reaction temperature rather than pressure.

ÖZET

KARBON MONOKSİT HİDROJENASYONU KATALİZÖRLERİNİN OKSİJENLENMİŞ HİDROKARBON ÜRETİMİ İÇİN İNCELENMESİ

Bu çalışmanın amacı karbon monoksit hidrojenasyonu yoluyla oksijenlenmiş hidrokarbon (özellikle etanol) üretimi için katkılı ve silika destekli rodyum katalizörlerinin performansının incelenmesi olarak belirlendi. Emdirme yöntemi kullanılarak iki farklı katalizör hazırlandı:1.5wt%Rh-2.6wt%La/SiO_2 ve 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2. Etkinlik testleri kapsamında, sıcaklık, basınç ve reaktörde kalma süresinin (W/F_{CO}) CO dönüşmesinin yanısıra metan, etanol ve karbondioksit seçimliliğine etkileri belirlendi. Katalizör yüzeylerinin mikro yapıları ESEM ve EDX teknikleriyle incelendi. Reaksiyon deneyleri, sistemin uzaktan kontrolu için programlanabilir kumanda ve yazılım ile donatılmış tam otomatik yüksek-basınçlı bir reaktör sistemi içinde entegre sabit yataklı bir mikro reaktörde gerçekleştirildi. Girdi ve ürün analizi için GC ve GC-MS olmak üzere iki on-line gaz kromatografı kullanıldı. Deneylerin ilk bölümü, sabit girdi bileşimi (mol bazında %10 CO, %20 H_2 ve fark N_2) ve 0.98 mg.min.μmol^{-1} reaktörde kalma süresi kullanılarak 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2 üzerinde gerçekleştirildi. Reaksiyon koşulları, 14-35 bar ve 240-315^{o}C arasında değiştirildi. İzleyen deneyler, çift katkılı Rh/SiO_2 için reaktörde kalma süresi 0.49-1.95 mg.min.μmol^{-1} aralığında değiştirilerek 25 bar ve 285^{o}C de gerçekleştirildi. Tek katkılı katalizör için deneyler de 0.98 mg.min.μmol^{-1} reaktörde kalma süresi ile aynı basınç aralığı kullanılarak 270-300^{o}C arasında yapıldı. Reaktörde kalma süresinin ve reaksiyon sıcaklıklığının artmasının yanısıra V katkı maddesinin eklenmesi de CO dönüşmesini olumlu yönde etkiledi. Tek-katkılı Rh-La/SiO_2 katalizörü önemli miktarlarda oksijenlenmiş hidrokarbon üretmezken, çift katkılı Rh-La-V/SiO_2 katalizörü ortamında etanol, asetik asit ve etil eter başlıca oksijenlenmiş hidrokarbonlar olarak belirlendi. Yüksek basınçların oksijenlenmiş ürün oluşumunu desteklediği görüldü. En yüksek etanol seçimliliği, CO dönüşmesi %9 düzeyinde iken %19 olarak elde edildi (270^{o}C, 35 bar). Bunu izleyen etanol seçimliliği ise, CO dönüşmesi %31 düzeyinde iken %15 olarak belirlendi (300^{o}C, 35 bar). Katalizör etkinliğinin basınçtan ziyade reaksiyon sıcaklığı tarafından kontrol edildiği gözlendi.

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F_{CO}	Carbon monoxide flow rate
ID	Internal diameter
MW	Molecular weight
N	Number of moles
T	Temperature
W_{cat}	Weight of catalyst
$\Delta\mathrm{H}_{298}$	Standard enthalpy of reaction

LIST OF ACRONYMS/ABBREVIATIONS

BET	Branauer Emmett Teller
BJH	Barrett-Joyner-Halenda
BOS	Birleşik Oksijen Sanayi
EDX	Energy dispersive X-Ray
ESEM	Scanning electron microscopy
GC	Gas chromatography
GC-MS	Gas chromatography-Mass Spectrometer
GHSV	Gross hourly space velocity

1. INTRODUCTION

Fischer-Tropsch technology can be briefly defined as the means used to convert synthesis gas containing hydrogen and carbon monoxide to hydrocarbon products. Catalytic hydrogenation of carbon monoxide is one of the direct routes for converting synthesis gas to useful chemical compounds. The Fischer-Tropsch products consist of a mixture of linear and branched hydrocarbons and oxygenated products such as alcohols, aldehydes, acids and ketones (Van der Laan, 1999).

The hydrogenation of CO to produce oxygenates is a field of interest due to their properties as gasoline blends and the necessity of finding alternative automotive fuels to meet legal requirements (Subramanian *et al.*, 2009). Among the potential end products, ethanol is particularly attractive since it serves as a clean alternative fuel, a gasoline blend and a hydrogen carrier. In addition, ethanol has been considered as a feedstock for the synthesis of a variety of chemicals, fuels and polymers (Chen *et al.*, 2011). As a fuel, ethanol has several ideal properties: it is nontoxic, easy to store and transport, producible from renewable sources and has a high energy density. One of the major obstacles for ethanol application in energy is the slow kinetics and low selectivity in ethanol synthesis (Choi and Liu, 2009).

There are currently no commercial plants producing ethanol or higher alcohols from syngas as an end product. It is well known that syngas conversion to C_{2+} oxygenates is often limited by the formation of methane. Low yield and poor selectivity for ethanol production from syngas stand as the major obstacles associated with the use of known catalysts (Spivey and Egbebi, 2007).

In 1975, the pioneering patent of the Union Carbide Corporation first reported the use of a rhodium catalyst for the reaction of syngas to C_{2+} oxygenates (i.e. a mixture of acetic acid, acetaldehyde and ethanol). Since then, intensive research has been carried out to further develop this kind of catalyst, aiming at high selectivity for one single product, such as ethanol (Yu-Hua *et al.*, 1987).

The key issue of catalyst development with respect to CO hydrogenation has been to control product selectivity. Extensive efforts have been focused on catalyst screening and mechanistic studies, aimed at developing highly selective catalysts for achieving a specific product distribution (Chuang *et al.,* 2005). Rhodium based catalysts have been developed for selective ethanol synthesis. Other C_2 oxygenates (i.e., acetaldehyde and acetic acid) as well as increased levels of methane production are also synthesized over these catalysts (Nirula 1994). Most Rh based SiO_2-supported catalysts have shown moderate activity and also good selectivity towards C_{2+} oxygenates during CO hydrogenation at high pressures (Chuang *et al.,* 2005).

The most relevant feature of Rh is its ability to adsorb carbon monoxide both associatively and dissociatively, allowing it to form both hydrocarbons and oxygenates. (Subramanian et al, 2010). Rhodium's unique activity for oxygenated products stems from its intermediate position in the periodic table between metals which do not dissociate CO (Ir, Pd, Pt) and those which easily dissociate CO under reaction conditions (Co, Fe). However, using unpromoted Rh, previous CO hydrogenation studies have observed strong selectivity to methane with minimal selectivity to oxygenates (Liu *et al.*, 2014). Literature shows that the activity and selectivity of Rh-based catalysts are increased by promoter(s), choice of support, synthesis method and Rh precursors. Optimum alcohol formation requires a balance between the rates of CO dissociation, hydrogenation and CO insertion. For example, promoters such as rare earth metals, alkali metals and other transition metals play an important role in these elementary steps (Abdelsayed *et al.*, 2012).

The objective of this study was to develop and test the performance of supported rhodium catalysts for oxygenated hydrocarbon production by CO hydrogenation, using a high-pressure reaction system. Lanthanum and vanadium were used as promoters. After preparing singly and doubly promoted Rh/SiO_2 catalysts, the effects of reaction parameters on the carbon monoxide hydrogenation reaction were examined.

Two different catalysts were prepared by sequential or co-impregnation to incipient wetness over SiO_2 as support material: 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2. The catalytic activity tests for both catalysts were conducted in a bench top reaction system under reaction conditions of 14-35 bar and 240-315°C. Effect of catalyst contact time (W/F_{CO}) was studied over 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2. The microstructures of catalyst surfaces were also studied via ESEM-EDX analysis.

Chapter 2 includes a literature survey on the CO hydrogenation reaction, potential catalysts (active metal, support and promoters), mechanism and influence of the operating conditions (temperature, pressure and feed gas composition) on the reaction performance. The experimental system, catalyst preparation and all the experiments carried out in this study are detailed in Chapter 3. The results obtained in the experiments are presented and discussed in Chapter 4, while the conclusions and recommendations for future work are given in Chapter 5.

2. LITERATURE SURVEY

A promising alternative to petroleum-derived fuels and chemicals is the utilization of coal, natural gas, and biomass to make synthesis gas for the production of alcohols and hydrocarbons. Indeed, large-scale facilities for the production of methanol and Fischer–Tropsch (FT) hydrocarbons continue to be built around the globe (Haider, 2009).

FT technology inevitably consists of three basic steps. These are synthesis gas preparation, Fischer–Tropsch synthesis (FTS) and product upgrading. Whatever the operating conditions the FT reaction always produces a wide range of hydrocarbon and oxygenated hydrocarbon products (Dry and Steynberg, 2004). Main products of are linear paraffins and olefins. Water is a primary product of the FT reaction, and CO_2 can be produced by the water gas shift reaction (Van der Laan, 1999). The overall reactions of FTS are summarized in Table 2.1.

Table 2.1 Major overall reactions in the Fischer-Tropsch synthesis (Van der Laan, 1999).

Main Reactions	
1. Paraffins	$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
2. Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
3. WGS reaction	$CO + H_2O \rightleftarrows CO_2 + H_2$
Side Reactions	
4. Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$
5. Catalyst oxidation/reduction	a)$M_xO_y + yH_2 \rightleftarrows yH_2O + xM$
	b)$M_xO_y + yCO \rightleftarrows yCO_2 + xM$
6. Bulk carbide formation	$yC + xM \rightleftarrows M_xC_y$
7. Boudouard reaction	$2CO \rightarrow C + CO_2$

2.1. Fischer Tropsch Technology

2.1.1. Synthesis Gas Production

In principle, syngas can be produced from any hydrocarbon feedstock. These include: natural gas, naphtha, residual oil, petroleum coke, coal, and biomass. The lowest cost routes for syngas production are based on natural gas (Spath and Dayton, 2003).

The technology used to prepare the synthesis gas used for Fischer-Tropsch synthesis can be separated into two main categories, gasification and reforming. Gasification is the term normally used to describe processes for conversion of solid or heavy liquid feedstock to synthesis gas, while reforming is used for conversion of gaseous or light liquid feedstock to synthesis gas (Dry and Steynberg, 2004).

For methane reforming, as with gasification, the feedstock usually reacts with steam and oxygen to produce hydrogen, carbon monoxide and carbon dioxide. Much less carbon dioxide is produced for reforming than for gasification. It can be removed from the synthesis gas for recycle to the reformer inlet. Preferably, it remains in the synthesis gas fed to the FT synthesis step (Van der Laan, 1999). The compositions of syngas obtained from various feedstocks and processes are listed in Table 2.2.

Table 2.2. Composition of syngas produced from different feedstocks by various processes (Van der Laan, 1999).

Feedstock	Process	Component (vol%)			
Natural gas, steam	SR	H_2	CO	CO_2	Other
Natural gas, steam, CO_2	CO_2 - SR	73.8	15.5	6.6	4.1
Natural gas, steam, O_2, CO_2	ATR	52.3	26.1	8.5	13.1
Coal/heavy oil, steam	Gasification	60.2	30.2	7.5	2.0
Coal, steam, O_2	Texaco gasifier	67.8	28.7	2.9	0.6
Coal, steam, O_2	Shell/Koppers gasifier	35.1	51.8	10.6	2.5
Coal, steam, O_2	Lurgi gasifier	39.1	18.9	29.7	12.3
SR= steam reforming, ATR= autothermal reforming					

The production of purified syngas typically accounts for 60–70% of the capital and running costs of the total plant. Methane is preferred to coal for syngas production. In methane reforming about 20% of the carbon is converted to CO_2, whereas with coal gasification the figure is about 50% due to coal's much lower hydrogen content. Since the cost of syngas is high, it is important that the maximum amount is converted in the FT reactors. This requires that the composition of the syngas matches the overall usage ratio of the reactions (Dry, 2002). The effect of selectivity on the H_2 to CO usage ratio is given in Table 2.3 for a few typical FT products.

Table 2.3. H_2/CO Usage Ratio of Fischer Tropsch Reactions (Dry and Steynberg, 2004).

Usage ratio of FT reactions

FT product	Reactions	H_2 to CO usage ratio
CH_4	$CO + 3H_2 \rightarrow CH_4 + H_2O$	3
C_2H_6	$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$	2.5
Alkanes	$n\,CO + (2n+1)H_2 \rightarrow C_n\,H_{(2n+2)} + n\,H_2O$	(2n+1)/n
Alkenes	$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$	2
Alcohols	$n\,CO + 2n\,H_2 \rightarrow C_n\,H_{(2n+1)}\,OH + (n\text{-}1)\,H_2O$	2

2.1.2. Fischer-Tropsch Synthesis

The performance of the FT synthesis depends on interrelated variables. Altering the operating temperature, the type of catalyst, the amount or type of promoter, the feed gas composition, the operating pressure or the type of reactor used, product distribution can be varied (Dry and Steynberg, 2004).

Currently there are two FT operating modes. The high-temperature (300–350^{0}C) process with iron-based catalysts is used for the production of gasoline and linear low molecular mass olefins. The low-temperature (200–240^{0}C) process with either iron or cobalt catalyst is used for the production of paraffins and high molecular mass linear waxes (Dry, 2002). The products by high temperature FT can be refined to gasoline and diesel, solvents and olefins while by low temperature FT, the primary products can be refined to special waxes or if hydrocracked and/or isomerized to produce excellent diesel, base stock for lube oils and a naphtha that is an ideal feedstock for cracking to light olefins (Gao, 2010).

The formation of the various products appears to be controlled by mechanistic and kinetic factors and the product distribution are very different from what would be expected from thermodynamic considerations. In comparison of the actual selectivity and calculated thermodynamic distribution under similar operating conditions reveals that the FT reactions under normal operating conditions are nowhere near thermodynamic equilibrium and the observed C_2 and higher products are produced in huge quantities relative to thermodynamic expectation. It appears that alcohols too are primary FT products (Dry and Steynberg, 2004).

Water is a primary product of the FT reaction. Carbon dioxide is the result of the subsequent WGS reaction and not the result of CO reacting with free O atoms on the catalyst surface. For a cobalt catalyst, which has little or no WGS activity, the overall H_2 to CO ratio under typical syntheses conditions is about 2. When iron based catalysts are used at low temperatures, the H_2 to CO usage ratio is lowered due to the simultaneous water gas shift (WGS) reaction (Subiranas, 2008).

2.1.3. Fischer-Tropsch Catalysts

All group VIII metals have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbons. Vannice and coworkers (1975) showed that the molecular average weight of hydrocarbons produced by FT synthesis decreased in the following sequence: Ru>Fe>Co>Rh>Ni>Ir>Pt > Pd. Among these catalysts ruthenium, iron, cobalt, and nickel have been considered for commercial production.

Ruthenium is a very active but expensive catalyst for the Fischer–Tropsch synthesis relative to Co and Fe. At relatively low pressures (*eg.* 100 bar) ruthenium produces much methane, whereas at low temperatures and high pressures, it is selective toward high molecular weight waxes (Van der Laan, 1999).

Under practical operating conditions nickel-based catalyst has high activity but produces too much methane, and additionally the performance at high pressure is poor, due to production of volatile carbonyls (Speight, 2011). On a relative basis taking the price of scrap iron as 1.0 the approximate cost of Ni is 250, of Co is 1000 and of Ru is 50000. Besides the very high price of Ru, the available amount is insufficient for large scale application. This leaves only Fe and Co as viable catalysts (Dry, 2002).

Both iron and cobalt are used commercially these days at a temperature of 200 to 300 ^{0}C and at 10 to 60 bar pressure (Van der Laan, 1999). Iron catalysts produce hydrocarbons and oxygenated compounds under different pressures, H_2/CO ratios, and temperatures up to 340^{0}C. Cobalt catalysts operate at a very narrow range of temperatures and pressures to avoid increase in methane selectivity. Iron catalysts seem to be more appropriate for conversion of biomass-derived syngas to hydrocarbons than cobalt systems because they can operate at lower H_2/CO ratios (Khodakov, 2007).

Although the activity at low conversion of two metals is comparable, the productivity at higher conversion is more significant with cobalt catalysts. The activity with iron based catalyst is negatively affected by the water produced, which inhibits the reaction while cobalt based catalyst does not have the same constraint (Jager and Espinoza, 1995). The cobalt based catalyst product selectivity is much more sensitive to the gas H_2/CO ratio, pressure and temperature than the iron based catalyst which is much more robust in use. Numerous studies have shown that introduction of a noble metal (Ru, Rh, Pt, and Pd) has a strong impact on the structure and dispersion of cobalt species, FT reaction rates and selectivity (Dry, 2002).

Various metals, including but not limited to iron, cobalt, nickel, and ruthenium, alone and in conjunction with other metals, can serve as Fischer–Tropsch catalysts. In addition to the active metal the catalysts typically contain a number of promoters (Speight, 2011).
CO hydrogenation produces paraffins, olefins, and oxygenated products such as alcohols, aldehydes, ketones, acids, and esters. Table 2.4 summarizes the Fischer Tropsch catalysts and product selectivity.

Table 2.4. Typical product selectivity of various CO hydrogenation catalysts

(Chuang *et al.*, 2005).

Species	Selectivity
I. Group VIII Metals	
Fe	(i) Linear and branched hydrocarbons–
	alkanes/alkenes and (ii) oxygenates:
	alcohols, aldehydes, esters, ketones
Co	Linear hydrocarbons – alkanes/alkenes
Ni	Methane and hydrocarbons
Ru	Methane, hydrocarbons and polyethylene at high pressures
Rh	C_{2+} oxygenates
Rd, Pt	Methanol
II. Mixed Oxides	
Zn oxide	Promotes methanol and ethanol formation on Rh
Zr, Mn, Alkali oxide	Promotes oxygenate formation on Group VIII metals
V oxide	Promotes ethanol formation on Rh
Th oxide	(i) Hydrocarbons–branched alkanes and
	(ii) oxygenates–methanol $(CH_3)_2O$, branched alcohols
Cr oxide	Methanol and branched alcohols
Cu/Zn oxide	Methanol
$CuCoCr_{0.8}K_{0.09}O_x$	Branched higher alcohols
III. Co-precipitated	
Na–Ni	Methane
Alkali-Mn-Ni	Methane, acetaldehyde
IV. Mo-Based Catalysts	
Mo	Hydrocarbons
Alkali–Mo sulfide	C_1–C_5 linear, primary alcohols
K–Co–Mo	C_1–C_4 alcohols

2.2. Hydrogenation of CO to Ethanol and Other Oxygenates

A large number of C_{2+} oxygenates are produced with high selectivity from syngas via modified FT synthesis. Fundamental understanding of the well-developed FT technology is crucial for catalyst design in ethanol synthesis because of the similarity to the catalytic conversion from synthesis gas to ethanol (Gao, 2010). Currently, ethanol is mostly produced via fermentation of biomass-derived sugars. At least three methods are known in the literature for the catalytic conversion of syngas to ethanol and higher alcohols: (i) Direct conversion of syngas to ethanol, wherein selective hydrogenation of CO occurs on a catalyst surface to produce ethanol directly. (ii) Methanol homologation, which involves reductive carbonylation of methanol over a redox catalyst surface to produce ethanol. (iii) A multistep ENSOL process, wherein syngas is first converted to methanol over a commercial methanol synthesis catalyst followed by methanol carbonylation to acetic acid in the second step and, then, subsequent hydrogenation of acetic acid to ethanol (Subramani and Gangwal, 2008).

Compared to other process, catalytic conversion of synthesis gas to alcohols is advantageous as this uses biomass instead of feed grains. Catalytic conversion of synthesis gas to alcohols is a continuous flow process, producing mixture of methanol, ethanol and other higher alcohols with comparatively higher yields (Surisetty *et al.*, 2011). Product distributions are influenced by temperature, feed gas composition (H_2/CO), pressure, catalyst type, and catalyst composition (Subramanian *et al.*, 2009).

2.3. Catalyst Types

The catalysts for the production of ethanol and other oxygenated hydrocarbons from syngas can be classified broadly into 4 categories (Haider *et al.*, 2009):

- Rh-based catalysts
- Modified methanol synthesis catalysts based on ZnO/Cr_2O_3 and $Cu/ZnO/Al_2O_3$
- Modified Fischer–Tropsch catalysts based on Co, Fe, and Ru
- Modified Mo-based catalysts

For the direct conversion of the syngas to ethanol and higher alcohols, Rh-based catalysts give the best ethanol selectivity, albeit the CO conversion is not optimal (Lin *et al.*, 2012). Modified Fischer–Tropsch catalysts give moderate ethanol selectivity but methane formation is dominant and methanol selectivity is high (Spivey and Egbebi, 2007). Mo-based catalysts have a high catalytic performance but they need a high reaction pressure (>50 bar) and usually have a long activity induction period during the reaction. (Liu *et al.*, 2013). Modified methanol synthesis catalysts give the high activity for ethanol formation in terms of CO conversion. However, methanol remains the dominant product on these catalysts (Egbebi, 2008).

The key issue of catalyst development with respect to CO hydrogenation has been to control product selectivity (Speight, 2011). Extensive efforts have been focused on catalyst screening and mechanistic studies, aimed at developing highly selective catalysts for achieving a specific product distribution (Chuang *et al.*, 2005).

2.3.1. Rh Based Catalysts

Rhodium based catalysts have been developed for selective ethanol synthesis. Other C_2 oxygenates (i.e., acetaldehyde and acetic acid) as well as increased levels of methane production are also synthesized over Rh-based catalysts (Nirula, 1994). These catalysts give the best ethanol selectivity, albeit at lower CO conversions. Methanol formation is very low but high CH_4 formation is thermodynamically favorable and seems inevitable (Spivey and Egbebi, 2007). Most of the attention on Rh-based catalysts for the synthesis of C_2 oxygenates (including ethanol and acetaldehyde) from syngas has been directed at studies of catalyst precursors, supports, promoters or additives and a new reactor system (Huang *et al.*, 2012).

Mei *et al.* (2010) investigated the ethanol synthesis by CO hydrogenation over SiO_2 supported Rh/Mn catalysts in the temperature range 255-305^{0}C with the gross hourly space velocity (GHSV) varies from 7500 to 15,000 L/L$_{cat}$-h. It was found that Mn promoter has a crucial role in improving the selectivity toward ethanol and other C_{2+} oxygenates by affecting the CO insertion. Methane selectivity was high, about 30–60%

and the selectivity of hydrocarbon, C_{2+} oxygenates and alcohols was 10–25%, 20–40%, and 10% respectively. The total CO conversion ranged from 6% to 60%. No significant conversion of CO to CO_2 via water gas shift reaction was found. Also, the effects of various promoters (M = Ir, Ga, V, Ti, Sc, Ca, and Li) over Rh/M alloy nanoparticles were investigated using density functional theory calculations. It was found that electronegativity difference between Rh and the promoter plays an important role in enhancement of ethanol selectivity by facilitating the CO insertion reaction.

Haider and coworkers (2009) explored the influences of support and Fe promoter loading on the activity and selectivity of Rh-based catalysts for the direct synthesis of ethanol from syngas. The reactions were performed at 270 ^{0}C, 20 bar, H_2/CO ratio of 1 and weight hourly space velocity of 8000 $cm^3/g_{cat}\ h^{-1}$. Although little ethanol was produced over 2 wt% Rh/SiO_2, a similar loading of Rh on titania was active for this reaction. 1 wt% Fe promoted catalyst exhibited 22% selectivity to ethanol, with methane being the primary side-product. Addition of Fe to Rh/TiO_2 also improved the selectivity to ethanol with the highest value being 37% for a sample with 5 wt% Fe. Although the influence of pressure and H_2/CO ratio was moderate over 2 wt% Rh–2.5 wt% Fe/TiO_2, higher temperatures increased methane production at the expense of ethanol and methanol. The CO conversion and ethanol selectivity was 12.2% and 27.9%, respectively. It was also noted that CO_2 was never observed as a reaction product. Evidently, the extent of the water–gas shift reaction was negligible under this reaction conditions.

The effects of temperature, pressure, and H_2/CO ratio on the performance of a 6% Rh–1.5% Mn/SiO_2 catalyst for CO hydrogenation in a microchannel reactor were investigated. The reaction was performed in temperature range between 265 and 300 °C and pressure between 20 and 54 bar using a H_2/CO ratio of 2 and GHSV of 3750 h^{-1}. The Rh–Mn/SiO_2 catalyst at 300 °C, 54 bar and GHSV of 3750 h^{-1} exhibited about 40% CO conversion, with an ethanol selectivity of about 44%. Increasing reaction temperature from 280 to 300 °C increased the CO conversion from about 25 to 40%, but the selectivity to methane also increased to 48%. It was noted that reaction temperature, rather than reaction pressure, has a strong influence on the product selectivity (Hu *et al.*, 2007).

The effects of La, V, Zn, Cu, Fe, Li and Ag promoters on Rh/SiO_2 catalysts in CO hydrogenation were investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at 230 ^{0}C and 1.8 bar. The promoters in this study represented different reported roles in the synthesis of oxygenates: Li (alkali metal, enhance the selectivity to oxygenates), Fe (transition metal, enhance hydrogenation), V (transition metal, enhance CO dissociation or CO insertion), La (lanthanide, enhance CO dissociation or insertion) and Cu, Zn, Ag (transition metals, enhance CO insertion). The doubly promoted Rh/SiO_2 catalyst promoted by both La and V exhibited the highest reaction activity and a good selectivity to ethanol and other C_{2+} oxygenates (Mo *et al.*, 2009a).

Furthermore Mo and coworkers (2009b) examined the effect of Fe on Rh–La–V/SiO_2. It was found that the addition of 0.8 wt% Fe, 2.6 wt% La, and 1.5 wt% V to 1.5 wt% Rh/ SiO_2 resulted in the highest selectivity to ethanol (34.6%) and a moderate activity compared to other promoted catalysts. It was stated that hydrocarbons made up the majority of the total products for the non-promoted catalyst. The addition of V resulted in the lowest selectivity for CH_4 and the addition of La led to an increase in the selectivity for ethanol. La and V promotion resulted in low selectivity for methane and methanol while the selectivity for CH4 being relatively unchanged for Fe–V–La promotion although some activity was sacrificed.

Gao *et al.* (2009a) investigated the kinetics of the formation of products over La, V and/or Fe promoted Rh/SiO_2 catalyst. It was found that, increasing H_2 pressure resulted in increased activities while increasing CO partial pressure had an opposite effect. The selectivity for CH_4 increases slightly and the selectivity for higher hydrocarbons decreased with increasing H_2 partial pressure. On the other hand, increased H_2 partial pressure may also decrease CO adsorption and dissociation, resulting in less chain growth. They claimed that the formation of ethanol involves a different pathway compared to the formation of higher hydrocarbons. Increasing CO partial pressure resulted in a decrease in CH_4 selectivity whereas the ethanol selectivity increased.

A study of the combined promoting effect of La and V oxides for ethanol formation during CO hydrogenation on silica-supported Rh catalysts at 230°C and 1.8 bar was conducted. Non-promoted and La and/or V promoted Rh/SiO_2 catalysts were characterized by TEM, CO chemisorption and FT-IR. It was found that, compared to non- promoted Rh/SiO_2, the singly promoted catalysts, $Rh\text{-}La/SiO_2$ and $Rh\text{-}V/SiO_2$, showed improved reactivity (3 fold) and better ethanol selectivity. However, the doubly promoted $Rh\text{-}La\text{-}V/SiO_2$ catalysts showed even higher activity (9 fold). The selectivity for ethanol and other C_{2+} oxygenates, with the selectivity of total C_{2+} oxygenates greater than 30%. The better performance of the $Rh\text{-}La\text{-}V/SiO_2$ catalysts was related to synergistic promoting effect of the La and V promoters. It was also noted that adding just more of each promoter by itself was not able to produce the enhanced catalytic performance (Gao *et al.*, 2009b).

In the study of Subramanian *et al.* (2010) CO hydrogenation to ethanol over 1.5 wt% Rh/SiO_2 promoted with La and/or V oxides. The effects of reaction conditions: temperature, H_2/CO ratio, space velocity and pressure on the activity and selectivity of these catalysts were examined. The selectivity of ethanol reached 51.8% (close to the highest literature value) at a CO conversion of 7.9% was achieved with a corresponding methane selectivity of 15.4% at 270°C, 14 bar and H_2/CO ratio of 2. Combined La/V promotion reduces methane selectivity and increases C_{2+} oxygenates selectivity compared to the singly promoted catalysts by increasing the rate of CO insertion.

Egbebi *et al.* (2010) examined the effect of adding 0.1 wt% Li to Rh/TiO_2 catalyst for CO hydrogenation at 270°C, 20 bar and space velocity of 52800 cm^3/g_{cat}-h. They found the products contained 55% methane, 17% ethanol, 3% methanol, 15% acetaldehyde and the rest 10% contained CO_2 and C_{2+} light hydrocarbons at 2.5% conversion of CO. The addition of Li also increased formation of C_2 oxygenates at the expense of methanol and methane.

Moreover Egbebi and Spivey (2008) investigated the effect of H_2/CO ratio and temperature on methane selectivity in the synthesis of ethanol over the same catalyst above. They found that increasing the H_2/CO ratio favored the selectivity for ethanol versus methane although both of them increased. The increasing the H_2/CO ratio increased ethanol selectivity while it decreased the total oxygenate selectivity. It may be caused by hydrogenation of acetaldehyde or a common intermediate.

Arakawa *et al.* (1985) developed a high performance catalyst, Rh-Ti-Fe-Ir/SiO_2, that produces ethanol with 50% selectivity under the condition of 50 bar, 260^0C and H_2/CO ratio is 1. The catalyst involved two types of promoters; one type was to increase activity and the other type was used for increasing selectivity. Adding Ir, the ethanol selectivity was increased three times but CO conversion is not changed. Besides, high amount of CH_4 formation was suppressed. By introducing Fe to Rh/SiO_2 the ethanol selectivity was boosted. Ti promotion increased the conversion however lots of hydrocarbon was produced.

By employing Al_2O_3 as the support (calcined at different temperatures) iron-promoted Rh catalysts were investigated for ethanol production. Temperature programmed surface reaction (TPSR), X-ray diffraction (XRD) and N_2 adsorption desorption techniques were utilized to characterize the catalysts. The experiments were carried out at 280^0C and 50 bar at a space velocity of 12500 h^{-1}. The space time yield (STY) and selectivity of ethanol increased obviously from 40.7 g/kg/h and 19.6% to 69.4 g/kg/h and 23.0%, respectively when calcination temperature of the support was increased from 400 to 500°C. With further increasing of the calcination temperature, the STY and selectivity of ethanol increased gradually. The methanol formation activity increased simultaneously with the ethanol formation activity, and selectivity variation of methane and methanol changed slightly. Also, it was claimed that the calcination temperature of the support had little effect on selectivity of ethanol to methane ratio (Chen *et al.*, 2011).

Burch and Hayes (1997) have studied CO hydrogenation reaction over the catalysts containing 2 wt% Rh and 0–10 wt% Fe_2O_3 supported on Al_2O_3 at 270°C and 10 bar. The addition of Fe_2O_3 suppressed CH_4 formation while increased the selectivity to ethanol. The 2 wt% Rh catalyst promoted with 10 wt% Fe exhibited a ethanol selectivity of about 50%. It was claimed that a close interaction between promoter and active metal is important for selective oxygenate synthesis. Increased rhodium promoter interface accommodate more adsorbed CO which is thought to be a carbon-bound to a rhodium atom, oxygen-bound to a promoter ion.

Fukushima and coworkers (1985) reported the role of Ir in improving the C_2-oxygenate selectivity on Rh-Ir/$Si0_2$ and Rh-Ti-Ir/$Si0_2$ catalysts. The experiments were performed at 20 bar, 250 ^{0}C,at space velocity of 6000 h^{-1} over 4.0 wt% Rh catalyst. It was found that Ir exhibited a modifying effect, suppressing the hydrocarbon formation and improving the selectivity for C_2-oxygenate formation (70% carbon efficiency) in CO hydrogenation. When Ir was added to Rh-Ti/SiO_2, the formation of CH_4 and higher hydrocarbons was dramatically suppressed, whereas the yields of total C_2- oxygenates (mainly as EtOH) were constant over a wide range of Ir added. The maximum selectivity for ethanol was obtained at Ir/Rh atomic ratio of 0.5 and the addition of higher amount of Ir suppressed the CO conversion. The CO conversion was 6.5 % with 35% ethanol selectivity at given reaction conditions.

Syngas was converted to ethanol and n-propanol fairly selectively using trimetal catalysts of Fe, Co and Rh on silica. These catalysts demonstrated high activity at 270°C and 62 bar and methane was the major byproduct. CO conversion was about 20 % with the selectivity of ethanol 11%. Increasing the temperature has little effect on the product distribution until about 300 ^{0}C, where methane yields increase dramatically (Norman and Holy, 1985).

Bhore *et al.* (1989) reported that Mo promoted Rh/Al_2O_3 catalyst system displayed exceptionally high activity for CO hydrogenation and high selectivity for formation of oxygenates. The experiments were conducted at 30 bar, H_2/CO ratio of 2, at GHSV of 3000 to 36000 h^{-1}, 200 to 250^{0}C. It was noted that Mo-modified catalysts were unique in their high activities and increased selectivity. The activity was increased 12-fold by addition of 7.5% Mo. A 4% conversion was obtained at 225^{0}C at 18000 GHSV and the selectivity to total oxygenates was 73%.

Watson and Somarjai (1981) studied hydrated and anhydrous Rh oxides as catalysts for the hydrogenation of CO at 6 bar and in the range of 250-350 °C. The anhydrous oxide reduced to metallic rhodium rapidly, while the hydrated oxide was quite stable under the reaction conditions. The hydrated oxide produces a high concentration of oxygenated hydrocarbons, mostly acetaldehyde in addition to C_1-C_5 alkenes and methane. Also the activation energies to produce methane, ethylene, and acetaldehyde, are all about the same, 26.2 kcal/mole indicating that these molecules form from a common precursor.

Kip *et al.* (1987) examined the promotion of silica-supported Rh catalysts in the hydrogenation of CO by molybdenum oxide and thorium oxide at 1.5 and 40 bar, GHSV of $40001/l^{-1}h^{-1}$, H_2/CO ratio of 3. The activity was greatly enhanced by the presence of both molybdenum oxide and thorium oxide. Thorium oxide-promoted catalysts had a high selectivity to C_{2+} oxygenates (48-57%), more than half of it being ethanol. At pressure of 1.5 bar the methane selectivity was high and the methanol selectivity was low. However, the C_{2+} oxygenate selectivity was considerably lower than in the high pressure case (21.5 versus 51.8%). It was noted that this is different from V promotion, where high C_{2+} oxygenate selectivity was also measured in the low pressure experiment. It is remarkable that the increase in pressure did not improve activity for ThO_2 promoted catalyst.

Bhasin *et al.* (1978) performed experiments at 200 to 350°C and 25 to 200 bar of total pressure, over Fe promoted 2.5% Rh/SiO_2. Gas hourly space velocities were chosen to give synthesis gas conversions below 10%. Selectivity to ethanol was around 30% at 300°C, 68 bar and H_2/CO ratio of 1. It was shown supported Rh produces oxygen-containing compounds, specifically acetic acid, acetaldehyde, and ethanol. Addition of Fe to the rhodium catalysts sharply reduced the yields of acetic acid and acetaldehyde. Ethanol became the principal two-carbon product and methanol appears as a major product. Hydrocarbon production remained low, at least up to an iron to rhodium mole ratio of unity.

Ojeda *et al.* (2004) investigated the effect of manganese (the Mn loading varies between 0 and 3.2 wt %) on 3 wt% Rh/Al_2O_3 catalysts for the synthesis of oxygenated compounds from synthesis gas. CO hydrogenation was performed at 260°C, 20 bar and space velocity of 6000 cm^3/g_{cat}-h. The selectivity for oxygenate was about 50%, with ethanol being the major oxygenate. The addition of Mn affected the selectivity ethanol with no significant effect on the other oxygenated compounds. It was noted that ethanol and acetaldehyde might formed by different reaction pathways since MnO promoted the formation of ethanol keeping unaffected that of acetaldehyde.

Following the H_2 reduction at 500^0C, hydrogenation of CO over $RhVO_4/SiO_2$ catalyst has been investigated. The $RhVO_4/SiO_2$ catalyst gave higher activity and selectivity to C_2 oxygenates than the unpromoted Rh/SiO_2 catalyst. CO conversion over the $RhVO_4/SiO_2$ catalyst was much higher than that of V_2O_5-Rh/SiO_2, and the yield of C_2 oxygenates was enhanced. The selectivity to C_2 oxygenates decreased with increasing of CO conversion because of the secondary reactions to form CO_2 and CH_4, but the yield of C_2 oxygenates increased. It was also found that the $RhVO_4/SiO_2$ catalyst could be regenerated by calcination or O_2 treatment at 700^0C after the reaction (Ito *et al.*, 1998).

Pan and coworkers (2007) involved developing a high performance catalyst that enhanced activity of Rh particles confined inside nanotubes for CO hydrogeantion to ethanol. The catalyst was prepared by introducing active components of Rh, Mn, Li and Fe as in a weight ratio of 1:1:0.075:0.05 into the carbon nanotubes by a wet-chemistry method. The overall formation rate of ethanol was obtained as 30.0 mol/mol^{-1} Rh h^{-1} under the reaction conditions of 320^0C, 30 bar and space velocity of 12000 h^{-1}. Also, the same composition of metals on a silica support was tested. The oxygenate yield was more than twice than that of silica supported catalyst. Also the selectivity to methane reduced to about 15% from 41% over on catalyst supported on SiO_2.

In a recent study with catalyst supported on multi-walled carbon nanotubes (MCNTs), 3 wt% Rh/CNTs were loaded with Mn promoter. The reactions were carried out at 290^0C, 20 bar and different syngas flow rates. The enhancement in the degree of metal–promoter interaction (higher promoter loading) led to an increase in the ethanol selectivity. The CO conversion was obtained between 4% and 15% while the selectivity ethanol varied 24% to 35% over 2 wt% Mn, 3 wt% Rh/ CNTs. The results indicated that the selectivity to ethanol decreased as the CO conversion increased. The author anticipated that decrease in selectivity stems from the production of a significant amount of CO_2. The increase in ethanol production resulted in a production of water as a source for the water gas shift reaction (Liu *et al.*, 2014).

Huang *et al.* (2012) investigated Mn promoted Rh nanoparticles as small as approximately 2 nm in a silica nanoparticle (MSN) framework. The carbon selectivity for

C_2 oxygenates (ethanol and acetaldehyde) reached its highest point (75,4%) at 270^0C and 30 bar whereas the selectivity for methane was 25.1% although CO conversion was only 9.8%, that is, lower than the 24.2 % conversion at 300^0C.

Yu *et al.* (2012) synthesized a novel SiO_2 by the Stöber method and used it as support of Rh–Mn–Li catalyst for C_2 oxygenate synthesis via CO hydrogenation. They suggested that the hydroxyl–metal interaction over the catalyst supported on novel SiO2 promoted the CO dissociation and CO insertion, leading to higher CO conversion and C_2 oxygenate selectivity. The experiments were carried out at 300^0C, 30 bar and gas hourly space velocity of 10000 cm^3/g_{cat}-h. The conversion was 14% with 47% C_2 oxygenate selectivity. The space time yield of C_2 oxygenates increased remarkably to 198.5 g/(kg·h).

In another study of Yu and coworkers (2013), the effect of Fe promoter on Rh–Mn–Li/SiO_2 catalyst for CO hydrogenation was investigated. The results showed that low loading of Fe (0.1 wt%) improved the reactivity and yield of C_{2+} oxygenates; however, the opposite effect appeared at the high values of Fe (>0.1 wt%). The CO conversion increased with the temperature, but the C_{2+} oxygenates selectivity decreased. Thus, the maximum of C_{2+} oxygenates yield appeared at 300^0C and dropped off sharply when the temperature was further increased. The selectivity to ethanol reached 27% and CO conversion was 19% at 300^0C. The decreased ratio of acetaldehyde/ethanol (AcH/EtOH) with the increased Fe amount suggested that Fe enhances hydrogenation ability and boosts the hydrogenation of AcH to EtOH.

In a recent study, Rh-Mn-Li catalysts supported on SiO_2, ZrO_2 and SiO_2-ZrO_2 mixed oxides with various molar ratios of Si/Zr were tested for the synthesis of C_{2+} oxygenates at 280^0C and 30 bar. Compared with pure SiO_2 and ZrO_2 supported catalysts, catalysts supported on SiO_2-ZrO_2 showed higher activity and C_{2+} oxygenates selectivity, in which Rh-Mn-Li/SiO_2-ZrO_2 (ratio of Si/Zr=1:3) exhibited the best yield of C_{2+} oxygenates. It is claimed that SiO_2-ZrO_2 enhances activity and the C_{2+} oxygenates selectivity due to its ability of CO dissociation and moderate ability of hydrogenation (Han *et al.*, 2013).

2.3.1.1. Mechanism and Kinetics. The direct catalytic conversion of syngas to ethanol is accompanied by side reactions, leading to a variety of products; methane, C_2–C_5 alkanes and alkenes, aldehydes, ketones and esters. Methanation is highly exothermic and consumes significant amount of H_2. The other side reaction is water gas shift wherein the H_2O formed readily react with CO to produce CO_2 and H_2. These reactions are:

Direct conversion: $2CO + 4H_2 \leftrightarrow C_2H_5OH + H_2O$ $\Delta H = -253.6$ kJ/mol ethanol (2.1)

Methanation: $CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta H = -205.9$ kJ/mol ethanol (2.2)

Water gas shift: $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -74.6$ kJ/mol ethanol (2.3)

The reaction mechanism for CO hydrogenation to ethanol over the Rh-based catalysts is very complicated. The general mechanism proposed by a number of researchers for the formation of ethanol and other oxygenates was summarized by Chuang *et al.* (2005) and all the possible pathways of the mechanism in a network is given in Figure 2.1.

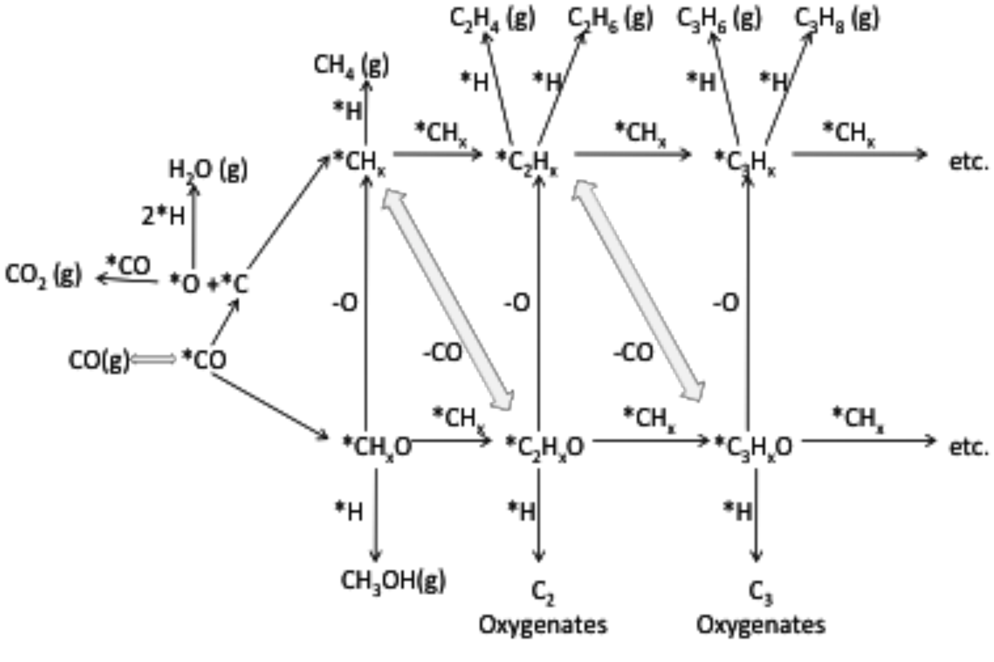


Figure 2.1. CO Hydrogeantion network (Chuang *et al.*, 2005).

CO dissociation and hydrogenation to produce CH_x species is the initial and crucial step for the synthesis of C_2-oxygenate on Rh-based catalysts. The direct hydrogenation of CH_x species produces CH_4. Alternatively methyl species undergo chain growth with another CH_x to produce C_{2+} hydrocarbons (Chen *et al.,* 2011). The formation of CH_x (x=1-3), has also been suggested by many researchers to be the rate-limiting step on different catalysts for CO hydrogenation (Gao *et al.,* 2009a).

The insertion of non-dissociated CO into the CH_x provides a common precursor of C_2 oxygenates, possibly a CH_3CO species on the catalyst and the subsequent hydrogenation gives oxygenates. On the other hand methanol is formed in the hydrogenation of non-dissociated CO, at different sites from the formation of C_2 oxygenates (Ichikawa and Fukushima, 1985).

Alternatively, ethanol also can be formed via acetaldehyde that is generated by CH_3 insertion into CO, followed by further hydrogenation. An other reaction route for ethanol is based on the insertion of CH_2 into adsorbed CH2–O species forming ethylene oxide (CH_2–CH_2–O) intermediates and then further hydrogenation into ethanol (Mei *et al.*, 2010).

The non-dissociated CO can react with water to form CO_2 (the WGS reaction). A suppression of CO dissociation and insertion will give rise to the existing of more non-dissociated CO, and this will in turn increase the extent of direct hydrogenation to methanol or the WGS reaction (Chen *et al.,* 2011).

Choi and Liu (2009) investigated the complex ethanol synthesis on Rh by density functional theory. They proposed that the selectivity to ethanol is controlled by methane formation and C-C bond formation between methyl species and CO.

Many kinetic studies have obtained positive H_2 pressure dependence and negative CO pressure dependence over Rh catalysts. Yin *et al.* (2003) studied the kinetics of CO hydrogenation for the synthesis of C_2 oxygenates over Rh-Mn-Li-Fe/SiO_2 catalyst. Increasing the hydrogen partial pressure favors the formation of ethanol rather than acetaldehyde. The carbon monoxide dependence orders for the formation of acetaldehyde and ethanol were 0.14 and -0.76 respectively. The formation of C_2 oxygenates, methanol and methane all exhibited negative order with respect to carbon monoxide.

Mori *et al.* (1990) determined the rate constants for C-O bond dissociation (k_{co}) and for the hydrogenation of surface carbon species (k_{ch}) by the pulse surface reaction rate analysis method. The reactions were carried out at 280^0C and 20 bar for the CO hydrogenation. They revealed that the high selectivity to C_{2+} oxygenates was observed for small k_{co} and k_{ch}. It was noted that C-O bond dissociation is the rate-determining step.

2.3.1.2. Supports. The effect of the support on the selectivity towards C_2 oxygenates has been thoroughly investigated. SiO_2 has been the most frequently used support, since Rh-supported on SiO_2 usually exhibit moderate activity and good selectivity towards C_2 oxygenates during CO hydrogenation, but its performance depends on the properties of the silica employed (Chen *et al.*, 2011).

Silica support is advantageous in terms of its high surface area, ample porosity and good stability. Also it was reported that catalysts supported on SiO_2-ZrO_2 mixed oxides showed higher activity and C_{2+} oxygenates selectivity. Other supports, such as oxides of Ti, Ce, V, Nb, Zr, have been reported to be favorable for the formation of C_2-oxygenate (Han *et al.*, 2013). Vanadium supported rhodium catalysts have been reported to have a high selectivity at low conversion for the production of ethanol (Gronchi *et al.*, 1994).

Ichikawa (1978) developed the catalyst prepared by the pyrolysis of Rh carbonyl clusters on weekly basic oxides such as La_2O_3, TiO_2 and ZrO_2. It was claimed that these catalysts showed high selectivity of the ethanol, acetaldehyde and methanol under atmospheric pressure and at 150-250^0C.

Chen *et al.* (2011) discussed the disadvantage of Al_2O_3 support for CO hydrogenation. The strong interaction between Rh and Al_2O_3 support leads to a lower Rh dispersion because of difficulty of reducing Rh completely. For the Al_2O_3 support, higher Rh or promoter loadings have to be used to achieve comparable activities to the silica-supported catalysts, so that very low Rh efficiency was resulted. Bhasin *et al.* (1978)

investigated the supports including silica gel, porous silica beads, alumina and activated carbon for Fe promoted Rh catalyst in CO hydrogenation. They reported that most active catalysts were those prepared on silica gel and silica beads. On the other hand alumina support was reported as inactive catalysts, possibly because of the difficulty with reducibility of rhodium on Al_2O_3.

Moreover recent studies showed that carbon nanotubes can be used as the catalyst support for Rh catalyst. They have shown exceptional catalytic performance. Carbon nanotubes as a support was reported to typically have high surface area (200–300 m^2/g), good mechanical and electronic properties as well as high thermal stabilities (Liu *et al.*, 2014; Pan *et al.*, 2007)

2.3.1.3. Promoters. Many elements including compounds of alkali, rare earths and transition elements have been tested over rhodium-based catalysts for CO hydrogenation.

Vanadium promoted Rh catalysts have been reported to have a high selectivity at low conversions for the production of ethanol. It increased the rate of CO dissociation which controls activity in CO hydrogenation (Koerts *et al.*, 1992). Ito and coworkers (2002) suggested that the role of the vanadium promoter is to enhance the CO dissociation, which leads to a high activity, and/or the CO insertion into the metal-carbon bond, which leads to the formation of C_2 oxygenates. Its promotion mechanism remains unclear.

Luo *et al.* (2001) studied the effect of addition of Sm and V to the Rh/SiO_2. The author asserted that Sm improve the dispersion of rhodium and vanadium ions of lower valence have a good capacity of hydrogen storage, and this can enhance the hydrogenation ability of the catalyst, as well as promoting the formation of ethanol. The addition of vanadium led to increases of the activities for C_2-oxygenates and of the selectivity of ethanol, and to a decrease of the selectivity towards the formation of acetic acid.

High ethanol selectivities can be reached with rare-earth-containing rhodium catalysts. More attention was paid to elements such as lanthanum and cerium. The effect of V promotion of Rh/SiO_2 for CO hydrogenation is similar to that of Ce. Cerium oxide is reported to be very effective for ethanol promotion when added to Rh/SiO_2, catalysts or used as support (70-80% ethanol selectivity below 10% CO conversion). In addition to its role in the activation of carbon monoxide towards hydrogenation, cerium oxide is also responsible for the reduction of acetaldehyde to ethanol (Kiennemann *et al.*, 1987).

Chuang and Goodwin (1985) reported the effect of various alkali species (Li, K, and Cs) on CO hydrogenation over $Rh/Ti0_2$ at reaction conditions of 250-330^{0}C and 10 bar. The activity of CO conversion was observed to decrease in the order: unpromoted >Li> K > Cs. The rates of formation for all the products decreased upon alkali promotion but the oxygenate selectivities were enhanced. Li generally suppresses methanation and hydrocarbon formation and increases selectivity to C_{2+} oxygenates (Egbebi *et al.*, 2010).

The promoter action of rare earth oxides such as La_2O_3, CeO_2, Pr_6O_{11}, Nd_20_3 and Sm_2O_3 on Rh/SiO_2 for syngas conversion to ethanol was investigated. The addition of especially CeO increases markedly the selectivity for production of ethanol (Yu-Hua *et al.*, 1987). The effect of lanthana promotion on $Rh/Si0_2$ was tested at 260^{0}C and 12 bar in CO hydrogenation reaction. It was stated that at low levels of lanthana addition the selectivity of CH_30H, C_2 oxygenates and C_2-C_4 hydrocarbons increased while selectivity for CH_4 decreased (Underwood and Bell, 1988). Mo and coworkers (2009a) tested the effects of different promoters on Rh/SiO_2 for the synthesis of ethanol via CO hydrogenation. They reported that La enhanced total CO adsorption, while V, Zn and Cu suppressed CO adsorption to different extents.

Besides promoters such as V, Sm and Mo have a positive influence on CO hydrogenation to ethanol. Mn also appears to be a favorable promoter (Haider, 2009). Manganese oxides not only improve selectivity of Rh catalysts for producing C_2 oxygenates but they also accelerate CO hydrogenation (Huang *et al.*, 2012). Adding Mn into Rh/SiO_2 increased the total activity by an order of magnitude. Both formation rates of methanol and C_{2+} oxygenates increased while the selectivity seemed to be insensitive to the Mn promoter (Mei *et al.*, 2010). Fukushima *et al.* (1985) reported that transition metals such as Mn, Ti and Zr exist most likely as oxides in the reduced Rh catalysts and provide a significant enhancement of CO conversion (ca. 10-50 times that with $Rh/Si0_2$), whereas the selectivities are still for C_2-oxygenates.

The promotion role of Fe is interpreted as boosting the hydrogenation of acetaldehyde to form ethanol. Fe promoted SiO_2 supported Rh catalysts was shown to be highly efficient for the hydrogenation of acetaldehyde which is thought to be an important secondary reaction in the catalytic production of ethanol (Burch and Hayes, 1997). Haider *et al.* (2009) also showed that the promotion of Fe substantially improved the activity of the catalysts and their selectivity to ethanol and other oxygenates.

The influences of various promoters on Rh-based catalysts for C_{2+} oxygenate synthesis is given in Figure 2.2.

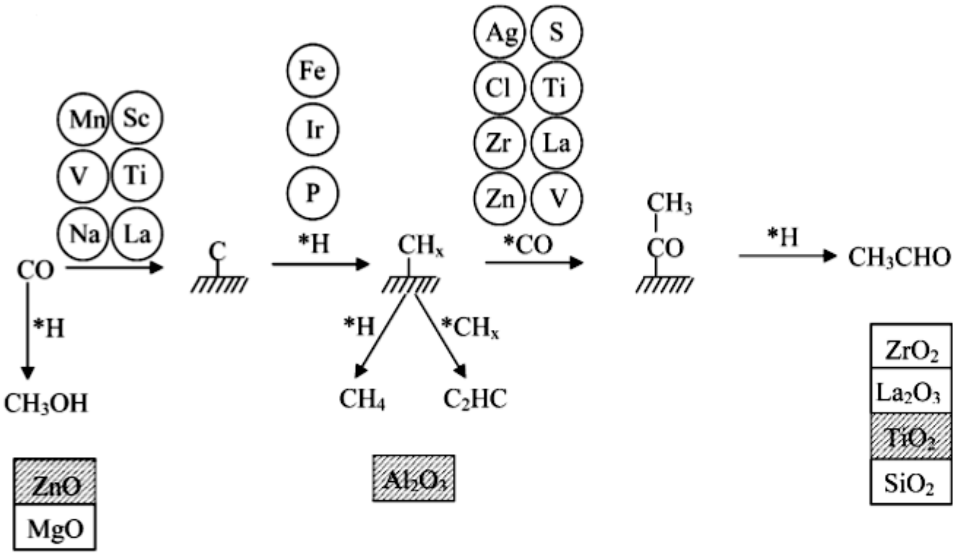


Figure 2.2. Support and promoter effects on C_2 Oxygenate Synthesis (Chuang *et al.*, 2005).

ZnO and MgO supports enhance the hydrogenation of adsorbed CO to form methanol. Mn, V, Na, La, Ti enhance CO dissociation; Fe, Ir, P boost hydrogenation of C species on the catalytic surface and Ag, Zn, La, V, Ti promote CO insertion. La and V promoters have effect on both CO insertion and dissociation (Gao, 2010).

<u>2.3.1.4. Influence of Temperature.</u> Egbebi *et al.* (2010) reported that increasing the temperature 260 to 270^{0}C reduced the total oxygenates, C_{2+} oxygenates and ethanol selectivities, while increasing methane formation over Li to Rh/TiO_2 catalyst in CO hydrogenation.

Mei *et al.* (2010) showed that how the selectivity to C_{2+} oxygenates decreased while the selectivity to C_{2+} alcohols increased with increasing temperature. Also, formation of higher hydrocarbon gases (ethane, propane, etc.) was significantly reduced as the catalyst was deactivated. The selectivity of methane increased, while the selectivity to C_{2+} oxygenates and alcohols decreases at elevated temperatures. The space time yields increased with temperature up to about 300 °C. It was noted that the activity of the Mn-Rh/SiO_2 catalyst decreased at 315 °C or higher.

Subramanian and coworkers (2010) examined the effect of reaction temperature over La and V promoted Rh/SiO_2 for ethanol synthesis via CO hydrogenation at 20 bar. It was stated that methanation must be kinetically limited in order to increase the ethanol yield and selectivity because methane is the thermodynamically favored product at all temperatures. The selectivity to ethanol increased from 18.6% to 39% as temperature changed 230 to 270°C. Also, at 270°C, the catalyst showed an ethanol selectivity 3.6 times higher than that for methane.

Haider and coworkers (2009) investigated process parameters of CO hydrogenation over Fe promoted Rh/TiO_2. They concluded that the conversion of CO increased with temperature, the selectivity to undesired methane increased at the expense of ethanol and methanol. They claimed that the influence of pressure on activity and selectivity was insignificant compared to the influence of temperature.

Hu *et al.* (2007) investigated the effects of pressure and temperature in the study of Mn-Rh/SiO_2 catalyst for CO hydrogenation in a micro channel reactor. It was noted that alcohol synthesis over Rh-Mn/SiO_2 was favorable at temperatures lower than 280^0C since at higher temperatures methane selectivity increased to around 48% and selectivity to ethanol decreased remarkably.

Ojeda *et al.* (2004) tested the effect of different reaction temperatures on CO hydrogenation over the Rh/Al_2O_3. The conversion increased with increasing reaction temperature as expected. Methane selectivity increased and the oxygenate selectivity decreased at higher temperatures, while that for the rest of hydrocarbons remained more or less unaffected.

Another study over Sm promoted Rh/SiO_2 catalyst showed that with increasing reaction temperature, the CO conversion and the ethanol yield increased, but the selectivity for oxygenates (methanol, acetaldehyde and ethanol) decreased, while the selectivity for C_{2+} hydrocarbons increased. It was claimed that there is rather a high tendency for oxygenates to dehydrate or hydrogenate at elevated temperatures (Yu-Hua *et al.*, 1987).

Watson and Somojai (1981) examined the CO hydrogenation over Rh based catalyst at 6 bar. Results indicated that raising the temperature 300 to 350^0C favored the production of shorter-chain hydrocarbons by increasing the rate of hydrogenation relative to that of chain growth. Conversely, lowering the temperature increased the total yield of oxygenated products. However below 250^0C, the rate of conversion was low to determine accurate oxygenates yields.

<u>2.3.1.5. Influence of Pressure.</u> Bhasin *et al.* (1978) reported that no oxygen-containing products were detected over Rh catalyst at atmospheric pressure. It is well established that Rh is a moderately active methanation catalyst at low pressures.

Mei *et al.* (2010) investigated the Rh based SiO_2 supported catalysts for ethanol synthesis by combining experimental study and theoretical modeling. It was declared that the ethanol selectivity increased while the methane selectivity decreased with increasing the total reaction pressure. They suggested that CO hydrogenation to ethanol on the Rh/Mn/SiO_2 catalyst is preferred under high-pressure condition. CO conversion also increased with the temperature but decreased with the total reaction pressure. The pressure changed the relative amounts of the product distributions it did not influence the essence of the chemistry occurring on the surface.

Egbebi (2008) stated that the equilibrium concentration of ethanol in CO hydrogenation is favored by increasing pressure although the effect weakens at higher pressure in a logarithmic fashion. The effect of pressure on the product selectivity is given in Figure 2.3.

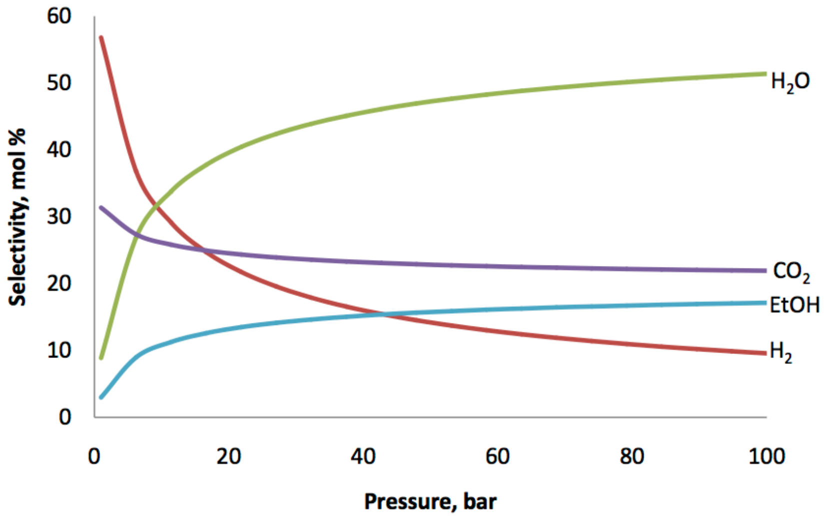


Figure 2.3 Equilibrium composition for the hydrogenation of CO; H_2/CO =2, 250°C, calculated using HSC Chemistry software (Egbebi, 2008).

2.3.1.6. Influence of H_2/CO ratio. Subramanian *et al.* (2010) reported that higher H_2/CO ratios may lead to the formation of hydrocarbons, particularly methane while at lower H_2/CO ratios, higher oxygenate selectivity is expected. When the H_2/CO ratio was raised from 2 to 4 over Rh-La-V/SiO_2 catalyst at 14 bar and 270 °C, the CO conversion increased and CO_2 selectivity decreased. It could be inferred that water gas shift reaction is not significant for higher H_2/CO ratio. The increase in CO conversion was accompanied by a increase in the selectivity to methane, but a sharp decline in the selectivity to higher hydrocarbons. It was observed that ethanol selectivity slightly decreased when the H_2/CO ratio was increased from 2 to 4.

The effect of H_2/CO ratio was studied by Hu *et al.* (2007). The experiments were carried out over Mn-Rh/SiO_2 catalyst in a micro channel reactor at 300^0C, 38 bar and GHSV of 3750 h^{-1}. When the H_2/CO ratio was reduced from 2 to 1, the CO conversion and the ethanol selectivity decreased while more C_{2+} hydrocarbons were produced. When H_2/CO ratio was raised to 3, CO conversion increased and CO_2 selectivity decreased and a slight increase in ethanol selectivity was observed. However, undesired product methane selectivity increased as well.

Egbebi and Spivey (2008) reported that increasing H_2/CO ratio has a small but positive effect on ethanol selectivity, whereas partial pressure of CO has relatively little effect. They also suggested that increasing the total pressure at constant H_2/CO ratio does not significantly affect selectivity to ethanol.

Bhasin *et al.* (1978) carried out experiments at 200 to 350°C and 25 to 200 bar with H_2/CO ratios ranging 1 to 10 over Fe-Rh/SiO_2. It was shown that the ratio of methane to the C_2 oxygenates decreased with decreasing H_2/CO ratio.

2.3.2. Modified Fischer Tropsch Catalysts

Modified Fischer-Tropsch catalysts, CuO/CoO/Al_2O_3 operate at temperatures between 260 and 340°C and pressures of 60 to 200 bar and catalyze the production of linear primary alcohols that follow ASF distribution. It is typically modified with Zn and alkali metals. The catalysts are designed for process conditions similar to those of low temperature methanol synthesis conditions: 50-150 bar, T = 220-350°C, with CO_2 also as a reactant (Xiaoding, 1987).

Kumar *et al.* (2012) used silica-supported Co–Pd catalysts with two different cobalt loadings: 2wt% (2Co–2Pd) and 10wt% (10Co–2Pd) to investigate activity/selectivity in CO hydrogenation. The studies showed that the 10Co–2Pd catalyst is more active for CO hydrogenation with high selectivity toward hydrocarbons, while 2Co–2Pd catalyst shows higher selectivity toward oxygenates, but considerably lower overall activity.

Among transition metals, cobalt is known to be very active for FTS while copper tends to form alcohols. This leads to the assumption that Co-Cu mixed oxide with alkali promoter could be a promising catalyst for syngas conversion into alcohols and hydrocarbons (He and Zhang, 2008).

Xiangen and coworkers (2012) examined the catalytic performance for CO hydrogenation over a series of silica supported Fe and Ni metal phosphides catalyst. With the FeP_x/SiO_2 catalysts (x denotes the molar ratio of P to metal), the product was a mixture of oxygenates containing methanol as the major component. 11.5% CO conversion was obtained with ethanol selectivity around 10% under conditions of 280°C, 50 bar.

In the research investigating the production of alcohols over Zn-Mn promoted Cu-Fe based catalyst, the results showed that the catalyst had high catalytic activity and high alcohol selectivity. The maximal CO conversion rate was 72%. The mainly hydrocarbon products were olefin and paraffin and the CH_4 selectivity was relatively low at the reaction condition of 48 bar, GHSV of 2000 h^{-1} with syngas of H_2/CO of 1. Furthermore, the C_{2+} oxygenates selectivity was 39 % in total alcohols at the temperature of as low as 220°C and reached 48 % at 280°C (Lu *et al.*, 2012).

Kintiachi *et al.* (1998) tested silica-supported bimetallic catalysts for synthesis of C_2 oxygenated compounds such as ethanol, acetaldehyde and acetic acid. $Ir\text{-}Ru/SiO_2$ catalyst exhibited the highest selectivity (21% at 300°C) to the C_2 oxygenated compounds. The addition of Li onto the bimetallic catalyst increased the selectivity up to 38.4 % at 280°C. High yield of C_2-oxygenates such as ethanol and acetaldehyde might have been caused by the interaction between CO-dissociative metal (Ru) and CO-undissociative metal (Ir).

$Co\text{-}Re/SiO_2$ catalyst possesses high activity for CO hydrogenation and produces oxygenates, especially ethanol with about 10% selectivity. By addition of Sr to this catalyst, the yield of hydrocarbons was depressed and the selectivity of ethanol was greatly increased to ca. 25%. It was reported that Sr depressed the formation of hydrocarbons and enhanced the formation of ethanol (Matsuzaki *et al.*, 1994).

2.3.3. Modified Methanol Catalysts

Modified methanol synthesis catalysts give the high activity for ethanol in terms of CO conversion. Most of the work reported on modified methanol catalysts for higher alcohols has been on Cu-based catalysts. Methanol remains the dominant product on these catalysts. The coupling reaction of two methanol molecules was identified as the mechanism to form ethanol over Cs doped Cu/ZnO catalyst. Alkali promotion of Cu-based catalysts has been found to increase with alkali atomic size, in the order Li, Na, K, Rb, Cs.

However, the effect of alkali doping on ethanol yield is not significant. For example the addition of 0.25mol% Cs to Cu/ZnO catalyst leads to an insignificant increase in ethanol yield while 1-propanol and isobutanol yields increase considerably (Egbebi, 2008).

Methanol synthesis catalysts modified by the addition of alkali metals: typically alkali promoted ZnO/Cr_20_3 catalysts which operate at high pressures and temperatures (260 bar and 350-400^{0}C) or low pressure Cu-based catalysts which have high productivities (0.45 g/g_{cat}-h) but suffer from selectivity drawbacks due to the formation of ketones, esters, etc. (The US Dept. of Energy, 1991)

Cu-based catalysts for the conversion of syngas to ethanol and higher alcohols are typically alkali-promoted/unpromoted combinations of Cu, Co, Zn, Al components. These catalysts produced promising results for higher alcohol synthesis in the temperature range of 280 to 300^0 C and at pressures about 55-70 bar. The most widely used H2/CO ratio was reported to be between 0.5 and 2. In general, promoters such as Cs or K on Cu/ZnO, $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ show the highest selectivity toward ethanol and higher alcohols (Gupta *et al.*, 2011).

The Octamix catalyst consists of 25-40wt% CuO, 10-18 wt% Al_2O_3, 30-45wt% ZnO and 1.7-2.5wt% K_2O; a Cu:Zn ratio of 0.4-1.9 and 3-18 wt% mix of promoters such as Cr, Ce, La, Mn, or Th operating under conditions of 250 to 400°C, 100 bar, a gas hourly space velocity of 1000-10000 h^{-1}, resulted in between 21-29% of the CO converted to alcohol with 29 to 45% of the alcohols being C_{2+} alcohols and 17 to 25% of the CO converted to CO_2 (Xiaoding, 1987).

Nunan *et al.* (1989) studied the synthesis of higher C_{2+} alcohols and esters over cesium-doped Cu-ZnO catalysts at 310°C, 76 bar, H_2/CO ratio of 0.45 and gas hourly space velocity of 3260 cm^3/g_{cat}-h. Under the reaction conditions employed, cesium increased the ethanol synthesis rate and provided an even greater enhancement in the rate of ethanol conversion to higher alcohols. CO conversion rate was about 5 to 20%.

Subramanian *et al.* (2009) investigated the Co–Cu nanoparticle catalysts for the synthesis of C_{2+} oxygenates from syngas via CO hydrogenation at temperatures ranging from 230^0C to 300^0C, 20 bar and 18000 cm^3/g_{cat}-h. It was observed that the Co–Cu mixed nanoparticles with higher Cu concentration exhibit a greater selectivity towards ethanol and C_{2+} oxygenates. The highest ethanol selectivity achieved was 11.4% with corresponding methane selectivity of 17.2% at 270^0C.

The effect of Cs and Ni promoters over Cu based catalyst was investigated at 250–350^0C under a total pressure of 30 bar and at a gas hourly space velocity of 2400 h^{-1}. Although catalysts produced methanol as a major product, the yield of higher alcohols (C_{2+OH}) formed over Cu/CeO_2 catalyst which was prepared by coprecipitation method was much larger than that over Cu/ZnO. By introducing Ni to $Cs\text{-}Cu/CeO_2$, the CO conversion increased from 22% to 38% and the mass ratio of C_{2+OH} to methanol in the products increased from 0.71 to 0.85. It was reported that Cu/CeO is a highly active catalyst and both Cs and Ni are effective for increasing the selectivity to alcohols (Liu, 2013).

Nonalkali promoters include the La, Mg, Fe, Ni, Cr, Co have also been used to promote the selectivity to higher alcohols over modified methanol catalysts. On the basis of the yields of C_2-C_4 alcohols, the most suitable promoter is Fe_2O_3 (Gupta *et al.*, 2011). The addition of Fe increased the selectivity to C_{2+} alcohols and decreased the selectivity to methanol however caused a reduction in catalytic activity (Xu, 2005).

2.3.4. Modified Molybdenum Catalysts

MoS_2-based, Co-Mo-S-based or Ni-Mo-S-based catalysts promoted with alkali promoters having excellent sulfur tolerance. It requires higher reaction pressures above 100 bar for ethanol synthesis compared with Cu-based catalysts (He and Zhang, 2008). To date modified methanol and modified FT catalysts have been more effective in the production of mixed alcohols; the sulfide-based catalysts tend to be less active than the oxide-based catalysts (Herman 2000).

The commercial potassium promoted MoS_2 catalysts to convert synthesis gas to alcohols were first developed by Dow and Union Carbide company (1984). The operating conditions for the process were at pressures in the range of 70-210 bar and temperatures of 250-300^{0}C with H_2/CO ratio of typically around 1.2. The product consisted of mainly straight-chain alcohols on the C_I-C_5 range. The total selectivity to C_{2+} alcohols was around 85% as CO pcr-pass conversion varied in the range of 20-25%. Molybdenum-based catalysts exhibit good water-gas shift activity, simplifying the removal of water from the product (The US Dept. of Energy, 1991).

Modified sulfide catalysts (mainly MoS_2) are used at temperatures between 260 and 350°C and at a pressure of 30 to 175 bar and result in the production of linear alcohols. Adding alkali metal suppresses the hydrogenation activity of the molybdenum active site and enhances alcohol formation. Cesium is the most effective alkali promoter although addition of potassium has also been extensively studied (Herman 2000).

Alkali-doped molybdenum sulfide catalyst was considered as one of the most promising systems for higher alcohol synthesis because of its high selectivity to alcohols and high activity of water-gas shift reaction and also resistance of sulfur poisoning in the feed gas. It was found that the Ni promotes the activity and selectivity to C_{2+} alcohols, however the selectivity to hydrocarbons also increased. Modified by Mn and Ni, MoS_2 catalyst showed high selectivity to alcohols because of the inhibition of formation of hydrocarbons and the selectivity to C_{2+} alcohols increased sharply at 100 bar and 300°C with H_2/CO ratio of 2.0 (Debao *et al.*, 2013)

Surisetty (2010) studied the Mo based catalyst for the production of higher alcohols, particularly ethanol from syngas. The effects of different loadings of active metal Mo, K as alkali promoter and metal promoter Co and Rh on higher alcohol synthesis were investigated using multi-walled carbon nanotubes (MWCNTs) as the catalyst support. The total yield of alcohols increased with increased Co content over MoS_2-K/MWCNTs catalysts, whereas, the maximum ethanol was observed on the catalyst promoted with 4.5 wt% Co. Over the Rh-promoted catalysts, the maximum total alcohol yield, ethanol selectivity and higher alcohols selectivity were observed on 1.5 wt % Rh promoted MoS_2-K/MWCNTs catalyst at 330°C, 90 bar and gas hourly space velocity of 38000 cm^3/g_{cat}-h.

The FT elements such as Ni and Co increase the alcohol yield and selectivity of higher alcohols of MoS_2 catalysts. The presence of Co in alkali-modified MoS_2 catalysts led to ethanol as the dominant product (Surisetty, 2011). Adding Co to alkalized MoS_2 catalysts increases the production of ethanol and other higher alcohols because Co promotes the homologation of methanol to ethanol (Forzatti *et al.*, 1991).

Co and Ni were found to be effective promoters to enhance the alcohol yield as well as C_2^+ alcohols selectivity of MoS_2 catalysts. Almost three-fold increase in the total alcohol was observed by introducing Co in $KMoS_2$ catalyst supported on clay. It was claimed that ethanol production rate was 129 mg/g_{cat}-h over K-promoted Co-MoS_2 catalyst at 300^0 C and 137 bar (Iranmahboob *et al.*, 2003).

Yong et. al (2007) studied Mo–Co–K sulfide-based catalysts promoted by rare earth metal salts (La, Ce, and Y). The performance for the selective synthesis of ethanol and mixed alcohols from syngas was evaluated and compared with that of the unpromoted catalyst. It was observed that the Mo–Co–K sulfide catalyst had a much lower CO conversion and ethanol distribution. In this study, also influence of molar ratio of La/Mo on the CO conversion and amount of ethanol were performed**.** Both CO conversion and ethanol distribution increased with the molar ratio of La/Mo.

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

All the chemicals used in catalyst preparation are listed in Table 3.1.

Table 3.1. Chemicals used in catalyst preparation.

Chemicals	**Formula**	**Grade**	**Source**	**Molecular Weight ($g.mol^{-1}$)**
Rhodium (III) nitrate solution, 10% (wt/wt)	$Rh(NO_3)_3$ hydrate	Extra Pure	Sigma-Aldrich	288.92
Lanthanum nitrate-6-hydrate	$La(NO_3)_3 \cdot 6H_2O$	Extra Pure	Riedel-de Haen	433.01
Ammonium meta-vanadate	NH_4VO_3	Extra Pure	Riedel-de Haen	116.98
Silica Gel Orange	SiO_2	Extra Pure	Sigma-Aldrich	60.08

3.1.2. Gases and Liquids

The gases required for the experiments include feed gases (carbon monoxide, hydrogen and nitrogen), GC sample carrier gas (argon), GC operational gas (argon), GC-MS operational gas (helium) and air (for automated pneumatic valve operation in the reactor system). The pressurized gas cylinders except argon and carbon monoxide were supplied by Linde Turkey, Istanbul. The argon cylinders were provided from Birleşik Oksijen Sanayii (BOS) and carbon monoxide was supplied by Hatgaz Turkey, Istanbul.

The applications and specifications of the gases in this study are listed in the Tables 3.2. For all solution preparations deionized water was used.

Table 3.2. Applications and specifications of the gases used.

Gas	**Application**	**Specification**
Carbon monoxide	Reactant, GC calibration	99.5%
Nitrogen	Reactant (inert), GC calibration	99.99%
Hydrogen	Reactant, Reducing agent, GC calibration	99.99%
Argon	GC carrier (reaction system)	99.995%
Argon	GC carrier	99.995%
Helium	GC-MS carrier	99.999%
Dry air	Valve Actuator	78.4% N_2 + 21.5% O_2
Methane	Product, GC MS calibration	99.9%
Carbon dioxide	Product, GC MS calibration	99.999%

3.2. Experimental Systems

The experimental systems used in this work can be classified into four groups:

- Catalyst Preparation System: Catalysts were prepared by sequential or co-impregnation to incipient wetness in this system.

- Catalyst Characterization System: The microstructure and surface morphology of the catalysts were analyzed scanning electron microscopy (ESEM-EDX).

- Bench Top Reaction System (BTRS): The Autoclave Engineers' BTRS-Jr-PC reaction system was used for catalytic activity tests. The system includes a tubular reactor, online sampling valve, mass flow controllers for automated delivery of reactants, back pressure regulator and gas liquid separator. A computer equipped with Programmable Logic Controller (PLC) and HMI software allows for the remote control of system functions.

- Product Analysis System: The composition of gases (H_2, CO, N_2) coming from the sampling valve located within the reactor system is analyzed by using on-line gas chromatography (GC). The reactor discharge is directed through the heated gas sampler to a gas chromatograph-mass spectrometer system (GC-MS) via heated lines to detect the products. The transfer lines to GC, GC-MS and the gas sampler of the GC-MS are heated to avoid condensation of products.

3.2.1. Catalyst Preparation System

Rh-La/SiO_2, Rh-La-V/SiO_2 catalysts were prepared by sequential or co-impregnation to incipient wetness of silica gel support. The system used for catalyst preparation includes a Retsch UR1 ultrasonic mixer which provides uniform mixing and contact of the solution with the support, a vacuum pump, a Masterflex computerized-drive peristaltic pump which is used for addition of the solution that will be impregnated, a vacuum flask, a beaker and silicone tubing as depicted in Figure 3.1.

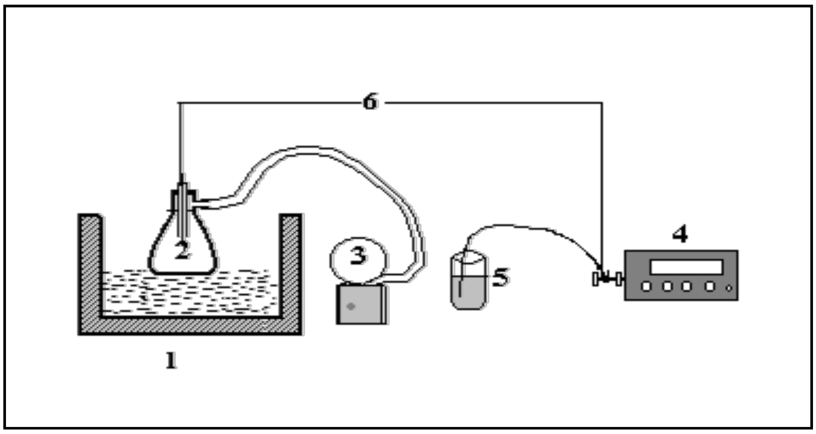


Figure 3.1. The impregnation system: 1.Ultrasonic mixer 2.Vacuum flask 3. Vacuum pump 4.Peristaltic pump 5.Beaker 6.Silicone tubing (Akın, 1996).

3.2.2. Catalyst Characterization System

The structural analyses of the catalyst samples were carried out through Backscattering Electron Scanning Electron Microscopy (SEM). The tests were conducted in a Philips XL 30 ESEM-FEG system, having a maximum resolution of 2 nm. The experiments were performed at the Advanced Technologies Research and Development Center of Boğaziçi University.

3.2.3. Catalytic Reaction System

The reaction system (Autoclave Engineers' BTRS-Jr-PC) that was used for catalytic activity tests includes a fixed bed micro-reactor integrated within a fully automated reactor system, which is completely encased within one bench top unit. The digital outputs from the system are connected to a computer from which all the settings (temperatures, pressure, gas flow rates, etc.) are controlled via Programmable Logic Controller (PLC) and software. The temperature, pressure and flow rates of gases are controlled by entering the desired set point on the software display screen. The system was constructed with all necessary tubing and auxiliary units in the laboratory. The reactor system and a close-up of the reactor within the oven chamber are presented in Figure 3.2 and Figure 3.3., respectively.

Figure 3.2. Fixed bed micro-reactor reaction system.

Figure 3.3. Interior oven chamber of reaction system.

The overall system can be divided into the following three major subsystems:

- Feed preparation section
- Reaction section and pressure control
- Feed/Product handling section

3.2.3.1 Feed Preparation Section. Three gas inputs (hydrogen, carbon monoxide and nitrogen) are connected to the reactor system and gases in pressurized cylinders are regulated by gas flow regulators (0-40 bar). The gas delivery rate is controlled by three mass flow controllers (Brooks Instruments Model number SLA5850S), one for each gas input. The flow rate ranges of the mass flow controllers are given in Table 3.3. All mass flow controllers are equipped with flow indicator controllers.

Table 3.3. Specifications of the mass flow controllers.

Gas Type	**CO**	**N_2**	**H_2**
Flow Rate Range	0-50	0-200	0-100
Max. Working Pressure	100	100	100
Temperature Limits (^{0}C)	0 to 65	0 to 65	0 to 65

Next, the feed gases enter the mixer where the incoming gases are combined and brought to a single stream leading to the reactor. The product gases are teed to the pressure gauge at this point where a pressure measurement is displayed. The reactant stream is diverted to the reactor via the reactor status valve.

All the automated valves in the BTRS reactor system are operated by pressurized air at 6 bar. The reactor, mixture tubing, switching valves and system tubing are all housed in a heated, insulated, stainless steel oven. In order to prevent condensation of product stream leaving the reactor, the oven is maintained at a temperature of 150^0C.

3.2.3.2 Reaction and Pressure Control Section. The system includes a stainless steel tubular with an internal diameter of 7.9 mm (0.25 inches). There are two reactors that were used alternatively and both of them have the same diameter. One has a length of 28 cm and the length of other is 43 cm. The reactor has a single zone electric resistance heater located on the exterior of a metal jacket. The electric heater zone has two Type "K" thermocouples which are connected to the PLC and are used to set and monitor reactor temperature. One is extending from the top of the reactor downward through the catalyst bed and the other is located on the furnace wall.

The maximum operating pressure of the system is 100 bar by design. The reaction system was pressurized with N_2 to the pressure set point entered on software display screen. Back pressure regulator is automatically controlled to maintain the desired pressure set-point within the reactor. The desired pressure set point is controlled by an automatic PID control loop. System pressure is monitored by an isolated pressure gauge. When pressurizing the reaction system, the same flow rate as that of the total feed (50 cm^3/min) was used. After the desired pressure was developed, the reaction was started as gas flow was switched into the feed gas mixture.

The reactor tube was filled with catalyst such that the catalyst occupies the center of the heated portion of the reactor tube. The catalyst bed was kept in place by inserting a plug of glass wool into the lower and upper ends. The bottom part of the reactor was filled with 1-mm glass beads to ensure that the catalyst bed stays in its fixed position during the reaction. The particular packing method used is given in Figure 3.4.

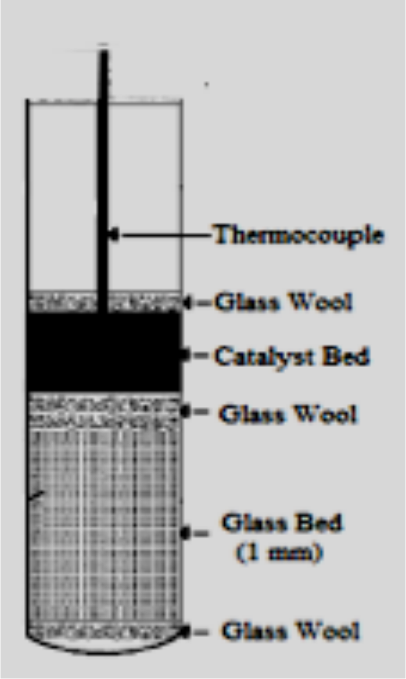


Figure 3.4. Schmatic diagram of packed-bed microreactor

3.2.3.2 Feed/Product Analysis Section. After leaving the reactor, the gases then flow into the Gas Liquid Separator (GLS) which is 150 cm^3 cylindrical vessels located outside the oven. The gases enter the GLS through a dip tube at the top of vessel and then exit through a tee at the top of vessel. The vessel is wrapped with copper coils for cooling water flow.

The product stream passing through GLS flows to a back pressure regulator. The product gases and vapors, now at a low pressure, exit the back pressure regulator and enter a reactant sampling valve. This valve is used for sampling of the process stream and uses argon carrier gas to deliver the sample to the GC. The sampling valve rotates between two positions: the collect mode and the transfer mode. In the collect mode the gases pass through the sampling loop and on to the reactant vent. In the transfer mode, the GC carrier gas pushes the product gas trapped in the loop to the heated transfer line and on to the GC. The heated transfer line is an insulated, stainless steel microbore tube about 3 meters long, maintained at 150^{0}C to avoid condensation of the gas stream. The desired set point of the heated line is entered on the software display screen.

The start-up experiments that utilized water cooling around the GLS showed that the conversion levels of the reaction were too low to accumulate sufficient amounts of condensate for offline GC-MS analysis. However, the product stream leaving the reactor must enter the gas liquid separator. Thus, it was decided to run experiments without passing cool water around the GLS vessel in order to send as much of the condensable products as possible for online GC-MS analysis. A three-way valve was installed to the reactant vent for diverting the product stream to the heated gas sampler of the GC-MS for online analysis. When the valve was switched to the heated line, the product stream was directed to the sampler via the heated line. To avoid condensation of the products before GC-MS, a 5 m-long heating tape was used to heat the line and a K-type sheathed thermocouple was placed along the heated lines and connected to a temperature controller. The heating tape was covered with ceramic wool insulation to prevent heat losses. The heated line was kept at approximately 100^0C.

The reactor status valve was used for performing feed gas analyses. This is a two-position multiport valve rotated by an air operator. The reactants flow through the reactor at offline position. When the status valve is at online position reactant stream bypasses the reactor, passing through all downstream components and the sampling valve to carry out the feed analysis. The schematic of the reaction system and the analytical equipment are shown in Figure 3.5.

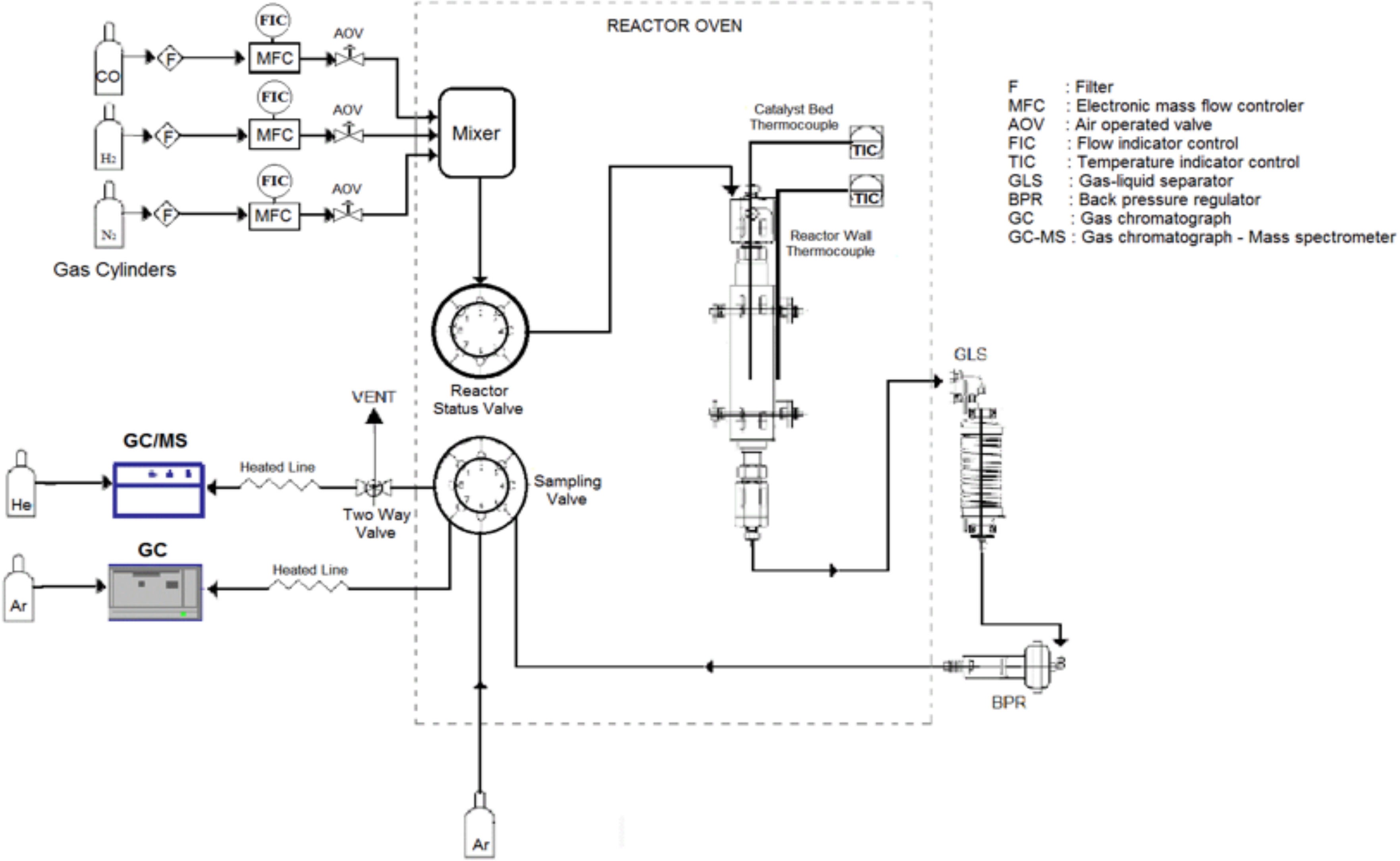


Figure 3.5. Schematic diagram of the microreactor flow system.

3.2.4. Product Analysis System

Two types of analytical systems were employed. For the identification of unreacted gases, a GC was used, and the products were analyzed by GC-MS. The feed gas streams (CO, H_2, and N_2) were analyzed using a Shimadzu GC-2014 temperature-controlled programmable gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). A carboxen packed column was used for detecting the components of gases after the reaction and was operated under argon as carrier gas. After leaving the back pressure regulator, the reactant stream enters the GC sampling valve located in the heated oven. GC carrier feed gas (argon) flowing through the reaction system pushes the gas trapped in the sample loop to the inlet of the carboxen column directly via the heated transfer line. The reactant analysis conditions used in the gas chromatograph are listed in Table 3.4.

The qualitative analysis of products consisting mainly of CH_4, CO_2, H_2O and C_2-C_5 hydrocarbons, acetaldehyde (C_2H_4O), ethanol (C_2H_5OH) and ethers is carried out using a Shimadzu QP2010 GC-MS with Rt-Q Bond capillary column, operated under helium as carrier gas. The operating conditions of the GC-MS are provided in Table 3.5.

Table 3.4. Analysis conditions for Shimadzu GC-2014.

Column Type	Packed Column
Detector Type	Thermal Conductivity
Column Temperature	40 °C (0 → 14 min) 40 → 150 °C (14 → 16 min) 150°C (16→ 24 min)
Injector Temperature	100°C
TCD Temperature	175°C
Detector current	50 μA
Carrier Gas	Argon
Carrier Gas Flow Rate	25 $cm^3.min^{-1}$
Column Packing Material	Carboxen 1000
Column ID & Length	3mm x 6 m
Sample Loop	1 cm^3

Table 3.5. Analysis conditions for Shimadzu GC-MS QP 2010.

Detector Type	Mass Selective Detector
Column Type	Rt Q Bond Capillary Column, Divinyl benzene
Column ID & Thickness &Length	0.53 mm x 20 µm x 30 m
Column Temperature	35 ˚C (0 → 5 min) 50 → 150 ˚C (5 → 7.3 min) 150˚C (10 min)
Injector Temperature	220°C
Column Flow	3 $cm^3.min^{-1}$ He
Sample Loop	1 cm^3
Split Ratio	50
MS Ion Source Temperature	220°C
Scan speed & scan range	769, 10-150 m/z

3.3. Catalyst Preparation

Rh-La/SiO_2 and Rh-La-V/SiO_2 catalysts were used in the experiments. The weight percentages of Rh based catalysts supported on silica gel were: 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2. Numbers preceding the symbol for an element indicate the weight percent of that element based on the weight of the silica gel support.

In previous studies using similar reactor geometries, catalyst particles of 250-344 µm in size were found to be sufficiently small to avoid internal mass transport effects arising from pore diffusion under the reaction conditions (Akın and Önsan, 1997). Therefore, catalyst particle size range was also selected as 255-344 µm in this work.

The steps in the preparation of the catalyst are summarized in Table 3.6.

Table 3.6. The steps for the catalyst preparation.

Application	Conditions
Calcination of support	500^0C, 4 hours
Sieving of support	45-60 mesh size
Washing of support	3 times with boiled water
Drying of support	115^0C, overnight
Calcination of support	500^0C, 4 hours in air
Keeping under Vacuum	30 min. prior to impregnation
Incipient to Wetness Impregnation	Impregnation of the aqueous solution of the precursors based on:1 g silica /1.3 cm^3 water into the calcined SiO_2 support
Mixing the slurry	90 min. under vacuum
Drying of support	90^0C 4 hours, 120^0C overnight
Calcination of catalyst	500^0C, 4 hours in air

3.3.1. Preparation of SiO_2 supported Rh-La catalyst

For lanthana promoted rhodium catalysts supported on silica, it was reported that the sequence of impregnation has an effect on catalytic behavior. Thus co-impregnation of the La with Rh was adopted since well-dispersed Rh particles are expected to form without being fully covered by La_2O_3 when this method is used (Borer and Prins, 1993).

La-promoted 1.5wt%Rh-2.6wt%La/SiO_2 catalyst was prepared by co-impregnation to incipient wetness of silica gel with an aqueous solution of $Rh(NO_3)_3$ hydrate and aqueous solution of $La(NO_3)_3 \cdot 6H_2O$ precursor of the promoter, followed by drying and then calcination in air.

Silica gel support was first calcined in a muffle furnace at 500°C for 4 hours to prevent the support from turning into gel form. It was ground and sieved to 45-60 mesh size (344-255 μm), washed 3 times using boiled distilled water to remove possible impurities and dried in a furnace at 115°C overnight and then calcined again in air at 500°C for 4 h before being used as a support.

First, a definite amount of silica gel support was put into the Büchner flask and was kept under vacuum in the first step. The support material in the vacuum flask was mixed under vacuum with an ultrasonic mixer for 30 minutes before impregnation. The vacuum pump was also kept on during the addition of the precursor solution since the trapped air in the pores of the support could prevent complete penetration of the solution.

Calculated amounts of aqueous solutions of $Rh(NO_3)_3$ hydrate and $La(NO_3)_3 \cdot 6H_2O$ were dissolved in the same beaker simultaneously in deionized water based on 1 g silica gel/1.3 cm^3 water to conduct the co-impregnation method. The resulting aqueous precursor solution was fed to the vacuum flask at a flow rate of 0.5 $cm^3.min^{-1}$ via silicone tubing using a peristaltic pump. The slurry was ultrasonically mixed during impregnation to maintain uniform distribution of the aqueous solution. After all the solution was fed, the mixing was continued for an additional 90 minutes. The resulting slurry was dried at 90°C for 4 h, and then at 120°C overnight before being calcined in air at 500°C for 4 h to obtain the 1.5wt%Rh-2.6wt%La/SiO_2 catalyst.

3.3.2. Preparation of SiO_2 supported Rh-La-V catalyst

The doubly promoted 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 was prepared by the sequential impregnation method. Firstly, the NH_4VO_3 solution was prepared in deionized water on the basis of 1 g silica gel/1.3 cm^3 water. The aqueous solution of NH_4VO_3 has to be prepared at elevated temperature because of its low solubility at room temperature (Gao *et al.*, 2009a). The calculated amount of NH_4VO_3 was dissolved in deinoized water at approximately 100°C just prior to impregnation of the support. All the other aqueous solutions were prepared at room temperature.

The same procedure as described above for singly promoted Rh-La/SiO_2 preparation was followed for impregnation of the aqueous NH_4VO_3 solution. After all the solution was fed, the mixing was continued for an additional 90 minutes. The resulting slurry was dried at 90°C for 4 h, and then at 120°C overnight before being calcined in air at 500°C for 4 h to obtain the 1.5wt%V/SiO_2 catalyst. After this step, co-impregnation to incipient wetness of silica gel with an aqueous solution of $Rh(NO_3)_3$ hydrate and $La(NO_3)_3 \cdot 6H_2O$ was carried out. The required amounts of aqueous solutions of $Rh(NO_3)_3$ hydrate and $La(NO_3)_3 \cdot 6H_2O$ were dissolved simultaneously in deionized water based on 1 g silica gel per 1.3 cm^3 water; the resultant mixture was impregnated on 1.5wt.%V/SiO_2, and after all the solution was fed, the mixing was continued for an additional 90 minutes. The resulting slurry was dried at 90°C for 4 h, and then at 120°C overnight before being calcined in air at 500°C for 4 h to obtain the 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalyst.

Four different batches (based on 5g SiO_2) of Rh-La-V/SiO_2 were prepared and mixed to obtain the major catalyst batch which was used in the experiments. All catalysts used during the experiments were diluted with inert α-alumina (600 mg) to avoid channeling and hot spots.

3.4. Catalytic Activity Experiments

3.4.1. Preliminary Work

Before starting the catalytic activity experiments, gas chromatograph was calibrated for CO and H_2 separately. Different concentrations of CO or H_2 in mixture with N_2 were sent through the reactor system to the chromatographic column under the conditions given in Table 3.4. Recording the corresponding retention time and the area under the peak, micromole versus peak area graphs were obtained for N_2, CO and H_2.

For quantification of products, calibrations of CO_2 and CH_4 were done by injecting known amounts of each species separately into the capillary column under the conditions given in Table 3.5. The corresponding peak areas were calculated by integrator software, and micromole versus peak area graphs were constructed. The amounts of CH_4 and CO_2

produced were calculated by using the chromatograms obtained at steady state conditions. The GC-MS software program performs automatic peak integration, and the amounts of the products are calculated according to the calibration curve prepared. Ethanol was quantified by using the ionization cross-section method taking methane calibration as reference. The method is explained in detail in Appendix A.

3.4.2. Reaction Tests

All catalysts prepared were reduced in situ under H_2 at 500°C for 2 hours before the reaction and kept under a stream of N_2 for 30 minutes before beginning to pressurize the system. The temperature program used for the reductive pretreatment and subsequent steps prior to the reactions is given in Table 3.7. After reduction, the temperature of the reactor was decreased down to the reaction temperature (240-315°C) in the course of nitrogen flow for 30 minutes and pressurizing. A stainless steel tubular down-flow micro reactor was used for determining the catalytic activities of the Rh based catalysts supported on silica.

The experiments were performed at three different pressures (14, 25 and 35 bar). The catalytic activity tests for carbon monoxide hydrogenation were conducted with the feed mixture of 10% CO, 20% H_2 by mole and N_2 as balance for all catalysts. One experiment was carried out with feed mixture containing 20% CO and 40% H_2. Different weights of catalysts (200, 250, 400 mg) were used during experiments to see the effect of W/F_{CO} ratio on CO conversion. The total flow rate, type of catalyst, reaction temperature, and pressure as well as catalyst weight were changed in order to see the effects of different parameters on the catalyst activity.

Table 3.7. Reduction program and steps prior to reaction for Rh based catalysts.

Segment	Starting and End Temperatures	Flowing Gas
Heating	Heating from 25°C to 500°C at 45 min.	N_2 with flow rate of 15 $cm^3.min^{-1}$
Fixing the temperature	Keeping constant at 500°C For 15 min.	N_2 with flow rate of 15 $cm^3.min^{-1}$
Reduction	Keeping temperature constant at 500°C for 2 hours.	H_2 with flow rate of 25 $cm^3.min^{-1}$
Cooling	Cooling down to reaction temperature	N_2 with flow rate of 10 $cm^3.min^{-1}$
Pressurizing	Following the 30 minutes of cooling segment, starting to pressurize	N_2 with flow rate of 50 $cm^3.min^{-1}$

The reaction conditions used are summarized in Table 3.8 and the list of experiments on Rh-La/SiO_2 and Rh-La-V/SiO_2 are given in Table 3.9 and Table 3.10, respectively.

Table 3.8. Reaction conditions for catalytic activity tests.

Parameter	Value
Catalyst Particle Size (mesh size)	45-60 (344-255μm)
Catalyst Amount (mg)	200, 250, 400
Reduction/Reaction Temperature (°C)	500/ 240, 255, 270, 285, 300, 315
Reaction Pressure (bar)	14, 25, 35
Reaction Total Flow Rate ($cm^3.min^{-1}$)	40, 50
W/F_{CO} Ratio ($mg.min.\mu mol^{-1}$)	0.49, 0.98, 1.53, 1.95

All experiments that were performed for testing the performance of the catalysts in CO hydrogenation are summarized in Tables 3.9-3.10.

Table 3.9. Reaction conditions for 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2.

Exp. No	Reaction Pressure (bar)	Reaction Temperature (°C)	W/F_{CO} ($mg.min.\mu mol^{-1}$)
1	14	240	0.98
2		270	
3		300	
4	25	240	
5		255	
6		270	
7		285	0.49
8		285	0.98
9		285	1.53
10		285	1.95
11		300	0.98
12		315	
13	35	240	
14		270	
15		300	

Table 3.10. Reaction conditions for 1.5wt%Rh-2.6wt%La/SiO_2.

Exp. No	Reaction Pressure (bar)	Reaction Temperature (°C)
1	14	270
2		300
3	25	270
4		285
5		300
6	35	270
7		300

3.4.2.1. Experiments on Rh-La/SiO_2 catalyst. Seven experiments were performed over the singly-promoted Rh-La/SiO_2 catalyst to examine the effects of different temperatures and pressures on CO conversion and product distribution The list of experiments conducted is given in Table 3.11.

Table 3.11. List of experiments on 1.5wt%Rh-2.6wt%La/SiO_2.

Exp. No	Reaction Pressure (bar)	Reaction Temperature (°C)	Catalyst Amount (mg)	Total Flow Rate (cm^3/min)	Feed Gas Composition in N_2 as balance	
1	14	270	200	50	10	20
2	14	300	200	50	10	20
3	25	270	200	50	10	20
4	25	285	200	50	10	20
5	25	300	200	50	10	20
6	35	270	200	50	10	20
7	35	300	200	50	10	20

3.4.2.2. Experiments on Rh-La-V/SiO_2 catalyst. The variation of CO conversion and product distribution with reaction temperature and pressure was studied over the doubly promoted Rh-La-V/SiO_2 catalyst; the effects of variation of total inlet flow of gases, gas composition and weight of catalyst on activity were also observed. The list of experiments conducted is given in Table 3.12.

Table 3.12. List of experiments on 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2.

Exp. No	**Reaction Pressure (bar)**	**Reaction Temperature (°C)**	**Catalyst Amount (mg)**	**Total Flow Rate (cm^3/min)**	**Feed Gas Composition in N_2 as balance**	
8	14	240	200	50	10	20
9	14	270	200	50	10	20
10	14	300	200	50	10	20
11	25	240	200	50	10	20
12	25	255	200	50	10	20
13	25	270	200	50	10	20
14	25	285	200	50	10	20
15	25	285	200	50	20	40
16	25	285	250	40	10	20
17	25	285	400	50	10	20
18	25	300	200	50	10	20
19	25	315	200	50	10	20
20	35	240	200	50	10	20
21	35	270	200	50	10	20
22	35	300	200	50	10	20

4. RESULTS AND DISCUSSION

4.1. Catalyst Characterization

4.1.1. Total Surface Area

The surface area, pore volume and pore size estimations of calcined silica gel support and freshly reduced 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalysts were reported in a previous study (Erol, 2011). Further addition of V to the single La promoted catalyst resulted in cumulative decreases in both total surface area and pore volume. Table 4.1 shows the results obtained by multi-point BET analysis and the BJH method on the basis of adsorption data.

Table 4.1. Total surface areas, pore volumes and pore radii of the SiO_2 support and promoted Rh-based catalysts (Erol, 2011).

Sample	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore Radius (Angstrom)**
Silica Gel	224.7	0.120	14.85
1.5wt%Rh-2.6wt%La/SiO_2	189.2	0.097	14.82
1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2	180.5	0.091	14.79

4.1.2. ESEM Analysis

The microstructure, morphology and composition of freshly reduced and spent catalysts were studied by environmental scanning electron microscopy (ESEM) coupled with energy dispersive X-ray analysis (EDAX). The 1.5wt%Rh-2.6wt%La/SiO_2 and the 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalyst samples were analyzed. Moreover, the metal dispersion on catalyst samples was examined.

ESEM images of the freshly reduced La promoted Rh/SiO_2 catalyst are shown in Figure 4.1 and Figure 4.2 at different magnifications. Additionally, micrographs of the spent catalyst are also presented in Figure 4.3. In these images, Rh clusters are seen over the silica support as tiny white and shining spots. Larger light gray areas belong to Al_2O_3 particles sitting on the catalyst surface. Since catalyst bed was diluted with alumina, it was not possible to obtain alumina-free catalyst for ESEM analysis.

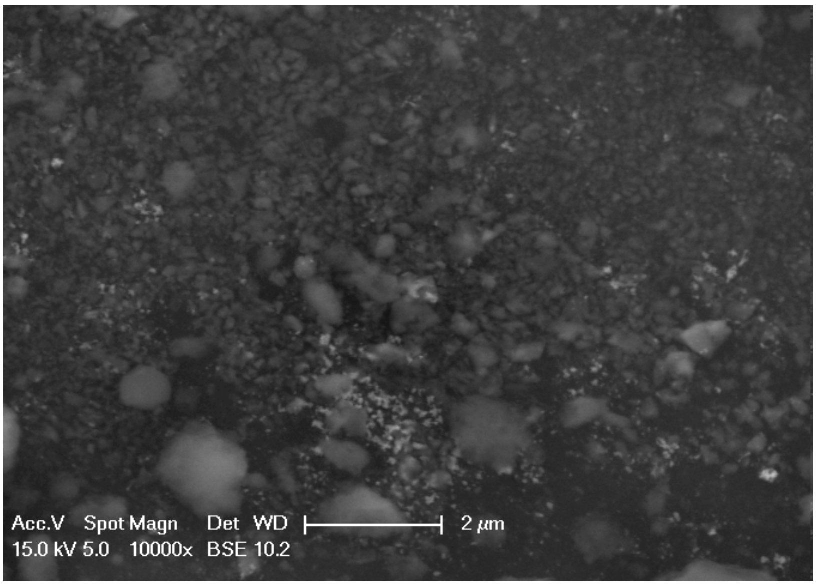


Figure 4.1. SEM image of freshly reduced 1.5wt%Rh-2.6wt%La/SiO_2 (10000x).

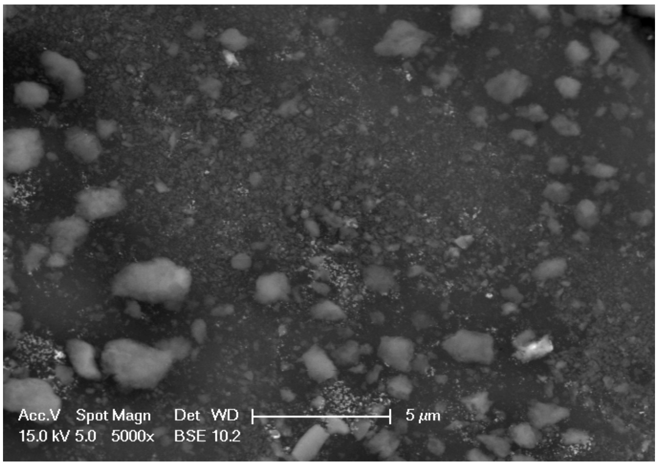


Figure 4.2. SEM image of freshly reduced 1.5wt%Rh-2.6wt%La/SiO_2 (5000x).

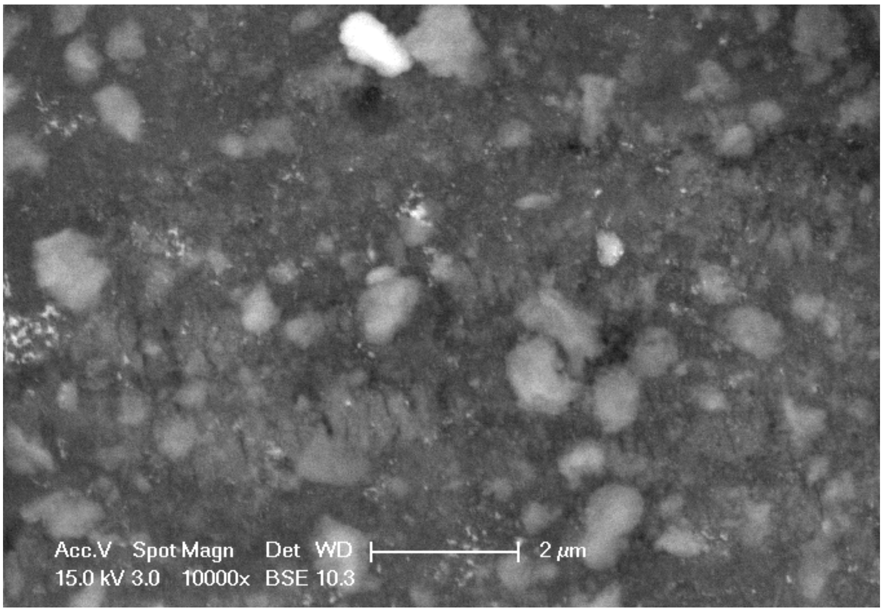


Figure 4.3. SEM image of spent 1.5wt%Rh-2.6wt%La/SiO_2 (10000x).

It is worth to note that lanthana coated areas were detected on the surface of some catalyst particles, although this is not a prevailing observation. Two representative micrographs of coated areas are provided as an example in Figure 4.4.

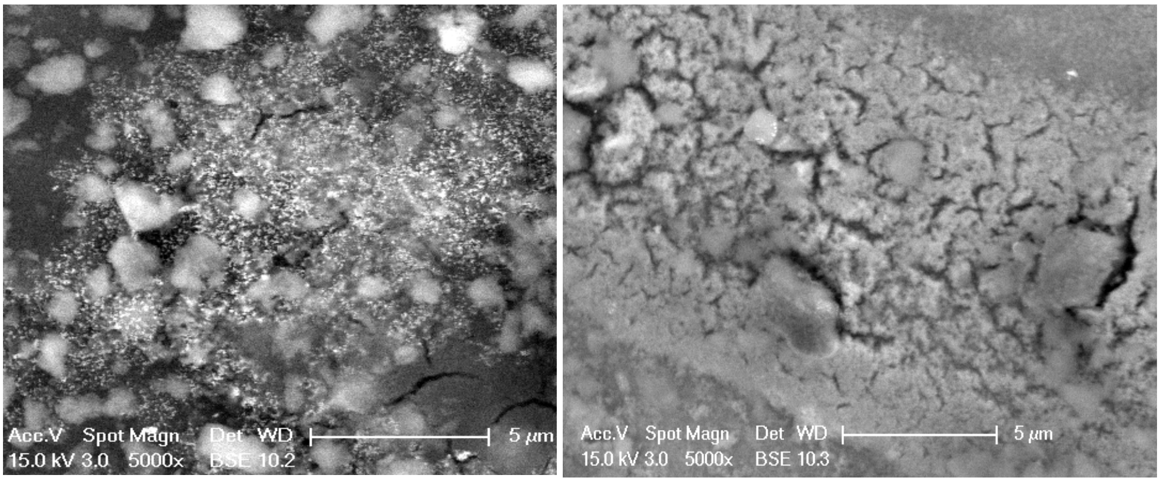
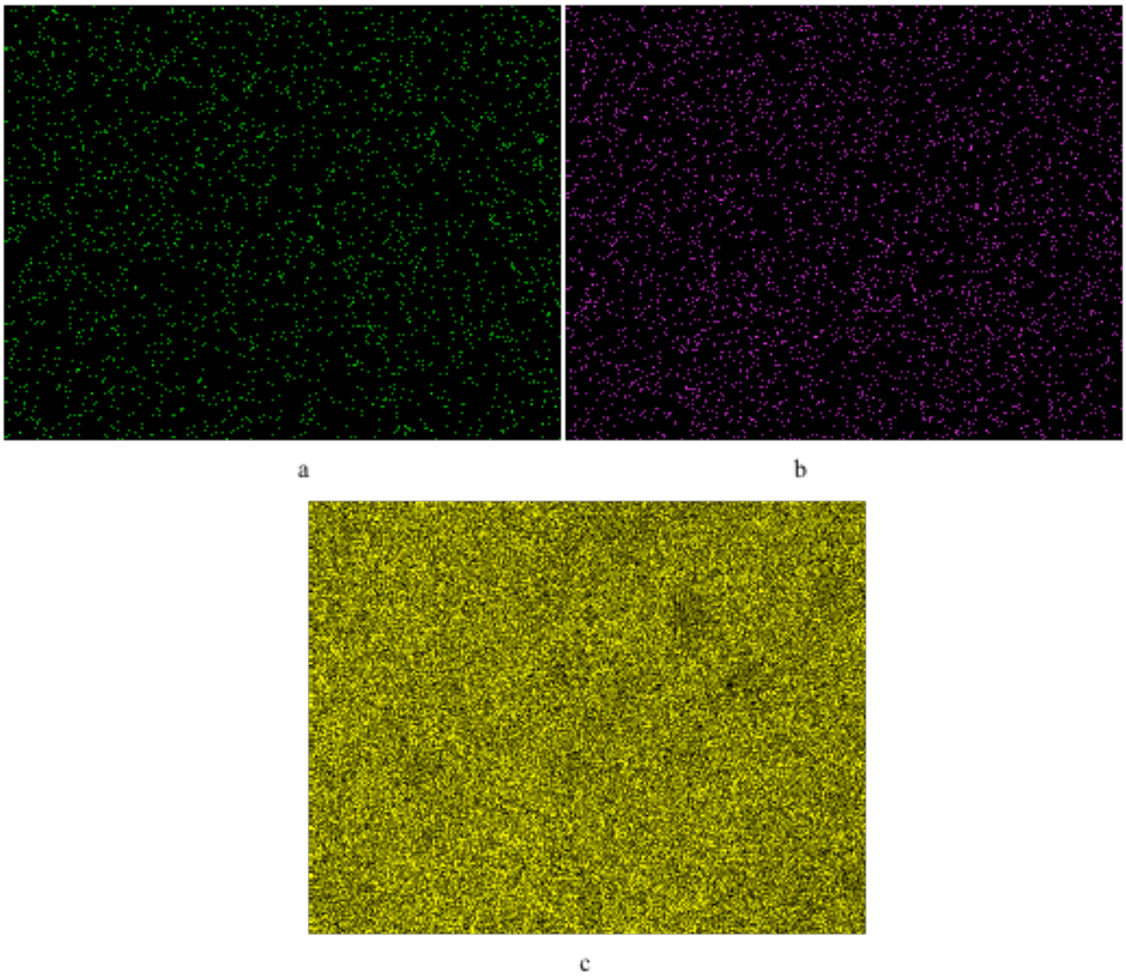


Figure 4.4. SEM images of lanthana coated areas over 1.5wt%Rh-2.6wt%La/SiO_2.

To understand the catalyst structure better, X-ray mapping of the surface was also conducted (Figure 4.5) which indicates that both Rh and La are well dispersed over the silica support in small particle sizes with some occasional clustering.



a

b

c

Figure 4.5. X-ray mapping of the 1.5wt%Rh-2.6wt%La/SiO_2 surface (a) La particles, (b) Rh particles, (c) Silica support.

ESEM micrographs of the 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalyst are shown in Figures 4.6 to 4.9. These images and the X-ray mappings presented in Figure 4.10 indicate that the double promotion by lanthanum and vanadium induces strong ability for the dispersion of Rh clusters on the silica support. Observations of different catalyst particles during ESEM analysis show that doubly promoted Rh-La-V/SiO_2 catalyst has better dispersion on the surface relative to the singly promoted catalyst.

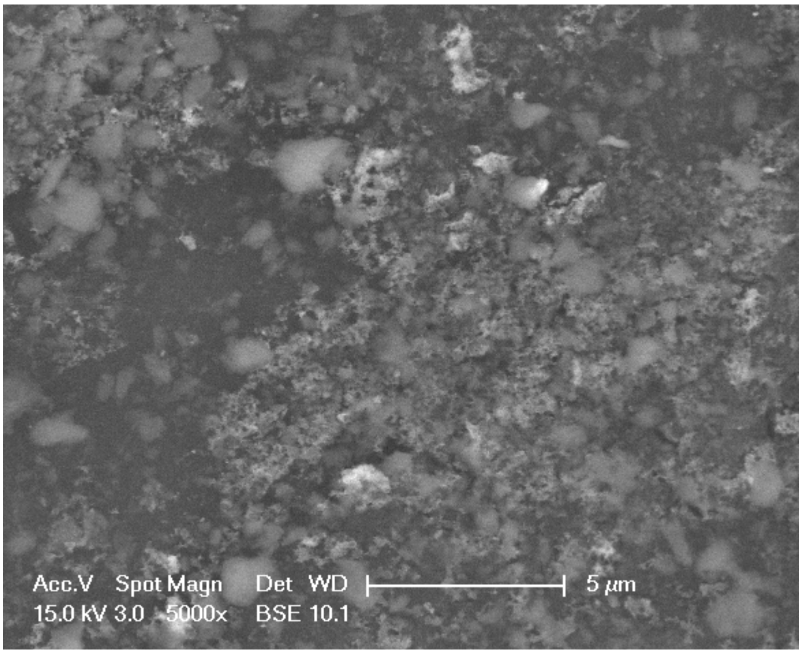


Figure 4.6. SEM image of freshly reduced 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 (5000x).

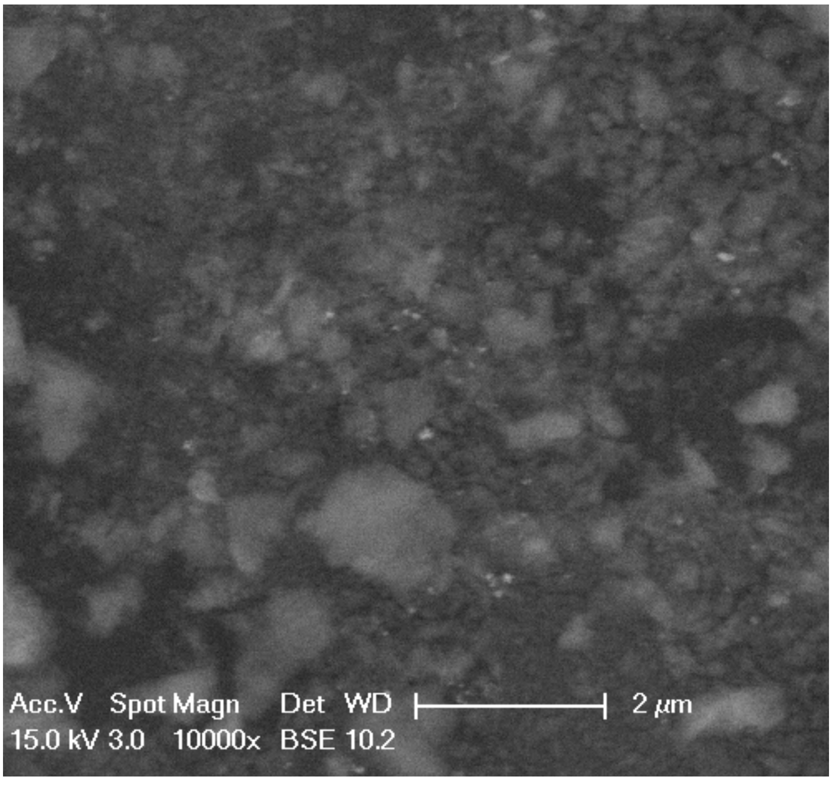


Figure 4.7. SEM image of freshly reduced 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 (10000x).

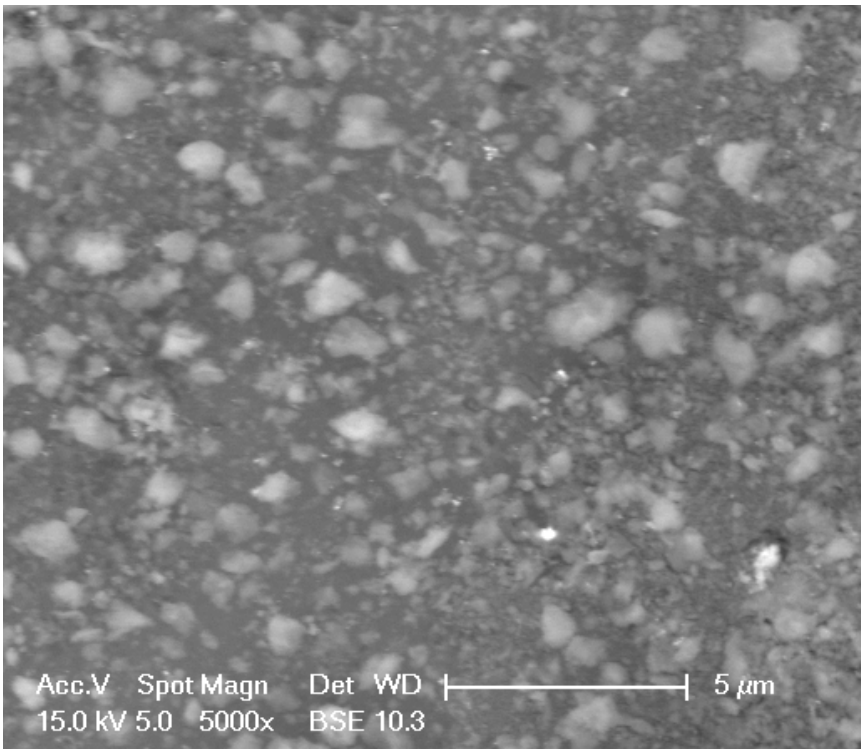


Figure 4.8. SEM image of spent 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 (5000x).

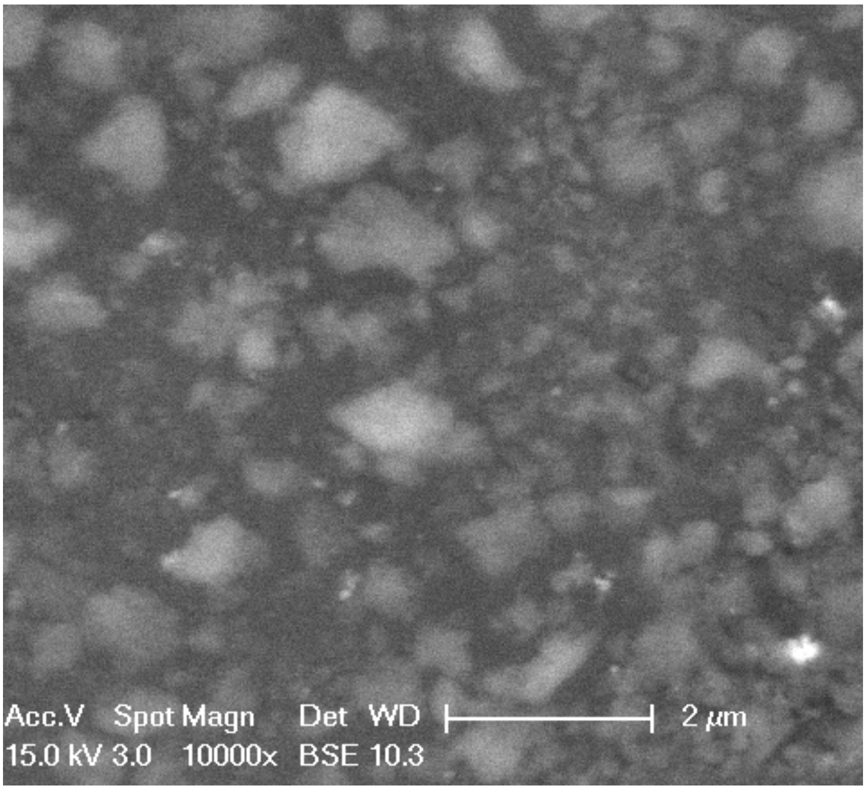


Figure 4.9. SEM image of spent 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 (10000x).

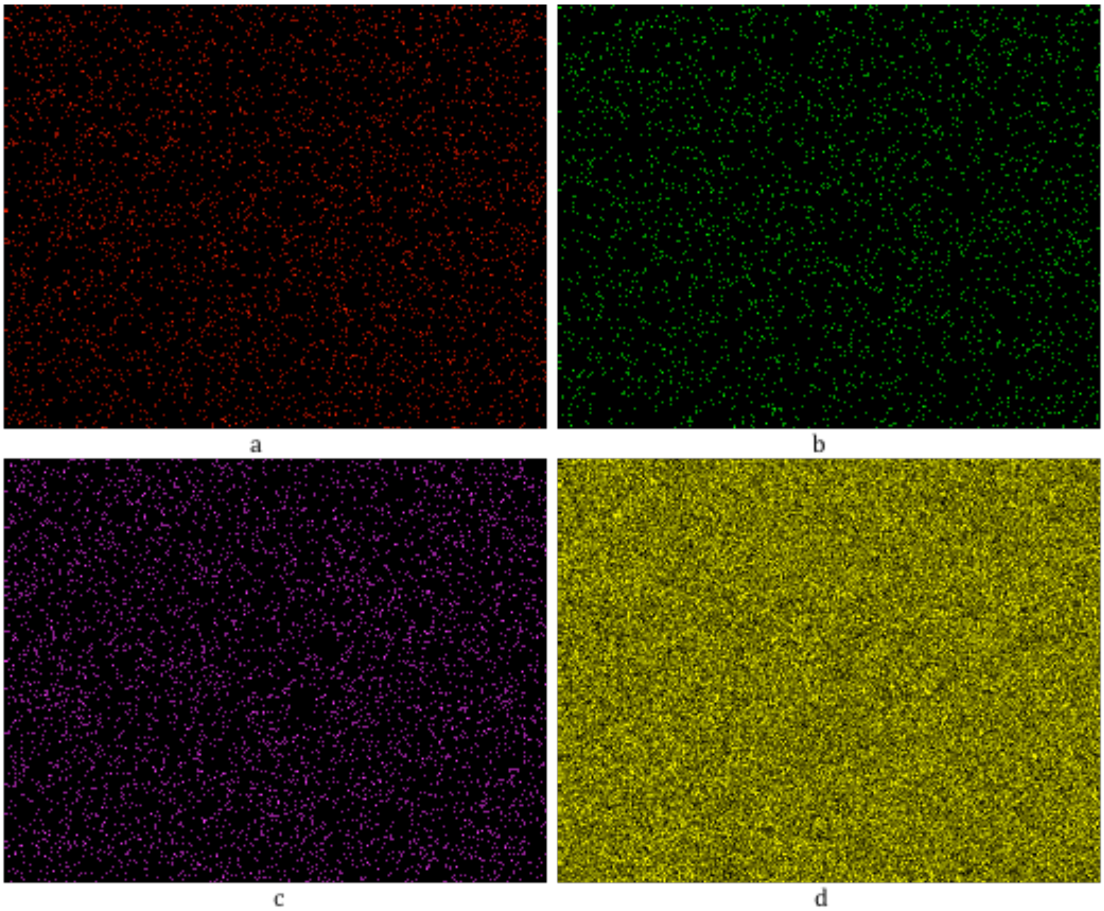


Figure 4.10. X-ray mapping of the 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 surface (a) V particles, (b) La particles, (c) Rh particles, (d) Silica support.

ESEM coupled with EDX was used for quantitative analysis of samples, and of different regions on each sample, to determine average metal loadings. Targeted and achieved metal loadings are presented in Table 4.2. It should be taken into account that there is a wider margin of error for low concentrations of elements. The figures provided in weight % need to be considered according to 20% relative error for 1-5% concentrations in EDX analysis (Bathaelt and Krüsemann, 2005).

Table 4.2. Targeted and achieved metal loadings by EDX analysis.

Catalyst	**Rh (wt%)**	**La (wt%)**	**V (wt%)**
1.5wt%Rh-2.6wt%La/SiO_2	1.61	2.31	—
1.5wt%Rh-2.6wt%La1.5wt%V/SiO_2	2.14	2.65	1.85

4.2. Carbon Monoxide Hydrogenation Reaction Experiments

The aim of this work was to test the CO hydrogenation activity and hydrocarbon product distribution obtained over promoted rhodium catalysts supported on silica. Two different catalysts were prepared by sequential and/or co-impregnation to incipient wetness of silica gel, namely 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2.

A parametric study was conducted to determine effects of reaction temperature, pressure, contact time (W/F_{CO}) on CO conversion as well as on the selectivity for methane, ethanol and carbon dioxide products. Parametric studies were initially conducted on the doubly-promoted 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2, using a fixed inlet composition of 10 mol% CO and 20 mol% H_2 with balance N_2 at a W/F_{CO} ratio of 0.98 mg.min.μmol^{-1}. Experiments were carried out in the 14-35 bar pressure and 240-300^{o}C temperature ranges in order to determine the more favorable reaction conditions. Subsequent experiments were performed at 25 bar and 285^{o}C using various W/F_{CO} ratios again over the doubly-promoted Rh-La-V/SiO_2, while the singly-promoted Rh-La/SiO_2 catalyst was tested at 270-300^{o}C using the same pressure range at a W/F_{CO} ratio of 0.98 mg.min.μmol^{-1}.

Literature shows that the activity and selectivity of Rh-based catalysts are increased by several factors such as promoter(s), choice of support material, synthesis method and Rh precursors used. Promoters such as rare earth metals, alkali metals and other transition metals play an important role in oxygenate and alcohol formation, affecting the rates of CO dissociation, hydrogenation and CO insertion mechanisms (Abdelsayed *et al.*, 2013). By far, the most widely studied catalysts for CO hydrogenation to oxygenates are based on Rh. Supported Rh has been known for decades to have the ability to selectively produce C_{2+} oxygenates such as ethanol, acetaldehyde and acetic acid from syngas (Bhasin *et al.*, 1978). Rh can also form methane, alcohols, or other oxygenates, by CO hydrogenation depending on the catalyst support, promoter(s) and the reaction conditions used (Ichikawa *et al.*, 1982).

Major products observed over the Rh-La-V/SiO_2 catalyst consisted of methane, carbon dioxide, C_2-C_4 alkanes, ethanol, acetic acid and ethyl ether. Small amounts of methanol, acetaldehyde, dimethyl ether, C_2-C_4 olefins, pentane and hexane were also detected by GC-MS analysis. In the case of Rh-La/SiO_2, products consisted basically of methane, carbon dioxide and C_2-C_4 alkanes whereas no significant quantity of any oxygenated hydrocarbon was observed.

The composition of the reactor outlet stream was measured during 310 minutes. In all experiments, steady state was reached after approximately 230 minutes as indicated by CO conversions and GC-MS chromatograms. The CO conversion results reported in this work are averages of the last three values obtained after 4 h on-stream. CO conversion was defined and calculated as follows:

$$\text{CO conversion (\%)} = \frac{[CO]_{INLET} - [CO]_{OUTLET}}{[CO]_{INLET}} \times 100 \qquad (4.1)$$

Product selectivity was calculated on the basis of % carbon selectivity. Carbon selectivity for a product was is the percentage of CO converted to this product in the total amount of CO converted, as also defined by various other authors (Huang *et al.*, 2012; Mochida *et al.*, 1988; Dry and Steynberg, 2004). The definition of product selectivity, where moles of a product containing N carbon atoms is denoted by C_N, is expressed as:

$$\text{Selectivity of } C_N \text{ (\%)=} = \frac{N \times C_N\,(mol)}{CO\ converted\,(mol)} \times 100 \qquad (4.2)$$

The values reported for ethanol selectivity may not reflect the actual values since the number of moles of ethanol was quantified approximately via the ionization cross section method (Fitch and Sauter, 1983) taking methane as a reference compound. Moreover, the total amount of ethanol produced may have not reached the GC-MS sampler due to possible condensation of the vapor product (boiling point of ethanol: 78°C) in gas liquid separator part of the reactor system. Although the reactor oven and the transfer line to the GC-MS system were heated, gas liquid separator vessel was at room temperature (located outside the oven) and the product stream had to pass through it. For instance, small amounts of liquid product were discharged from the gas liquid separator unit at the end of the reaction conducted under the conditions of 25 bar and 315°C.

4.3. Effect of Temperature and Pressure on the Activity and Selectivity of the La-Rh/SiO_2 Catalyst

A parametric study was conducted on the singly-promoted 5wt%Rh-2.6wt%La/SiO_2 catalyst to determine effects of reaction temperature and pressure on activity as well as product selectivity. Experiments were performed using a fixed inlet composition of 10 mol% CO, 20 mol% H_2 with balance N_2 at a W/F_{CO} ratio of 0.98 mg.min.μmol^{-1}. Reaction tests were conducted in the range of 14-35 bar at 270-300°C. CO conversions achieved on Rh-La/SiO_2 are presented in Table 4.3. Methane and carbon dioxide productions as well as their selectivity values were calculated according to peak areas obtained in GC-MS analysis, and the results are shown in Table 4.4.

Table 4.3. CO conversions over Rh-La/SiO_2 at different temperatures and pressures

Pressure (bar)	**Temperature (^{0}C)**	**CO conversion (%)**
14	**270**	1.2
	300	7.5
25	**270**	2.5
	285	6.9
	300	8.4
35	**270**	3.8
	300	10.9

Table 4.4. CH_4 and CO_2 selectivities and production rates over Rh-La/SiO_2 at different temperatures and pressures

Pressure (bar)	**Temperature (^{0}C)**	**CH_4 Production (µmoles/g_{cat}/s) (x100)**	**CO_2 Production (µmoles/g_{cat}/s) (x100)**	**CH_4 Selectivity (%)**	**CO_2 Selectivity (%)**
14	**270**	3.3	2.0	23.5	13.9
	300	48.3	22.9	57.4	27.2
25	**270**	4.3	3.1	23.1	16.1
	285	31.2	15.4	43.1	21.3
	300	48.8	26.9	55.2	30.4
35	**270**	4.7	3.9	15.3	12.5

As for CO conversion, it is evident in Table 4.3 that CO conversion values were quite low even for the experiment conducted at 35 bar and 300°C. The highest CO conversion reached on 1.5wt%Rh-2.6wt%La/SiO_2 was only 11%, which is almost one-third of the conversion (31%) achieved over 1.5wt%Rh-2.6wt%La1.5%V/SiO_2 under same reaction conditions. It is reported that doubly promoted Rh–La–V/SiO_2 catalysts exhibit much higher activity (up to 9 times) compared to non-promoted Rh/SiO_2 (Gao *et al.*, 2009b). The better performance of Rh–La–V/SiO_2 catalysts appears to be due to a synergistic promoting effect of the combined lanthana and vanadia additions through intimate contact with Rh. Use of just one promoter by itself was not able to produce the enhanced catalytic performance (Gao *et al.*, 2009a). It is reported that the La and V doubly promoted catalyst shows both new adsorbed CO species and increased desorption rate/reactivity of the adsorbed species during CO hydrogenation due to a synergistic promoting effect of La and V (Mo *et al.*, 2009a).

The activity of the catalsyt was predominately controlled by reaction temperature rather than pressure; also, changing the pressure and temperature did not cause any dramatic impact on product selectivity. Major products were basically methane, carbon dioxide and C_2-C_4 alkanes, while no significant amount of oxygenated hydrocarbon was observed in the GC-MS chromatograms. Only trace amounts of ethanol, methanol, acetaldehyde or ethyl ether were detected over the Rh-La/SiO_2 catalyst.

Experimental results obtained with 1.5wt.%Rh-2.6wt.%La/SiO_2 catalyst in the present study at different pressures are compared in Table 4.5 with some analogous data reported in the literature.

Table 4.5. Comparison of CO hydrogenation performance of 1.5wt%Rh-2.6wt%La/SiO_2 at 270°C and H_2/CO=2 at different pressures.

P (bar)	**Space Velocity (cm^3/h/gcat)**	**Rate of CO conversion (µmoles/gcat/s)**	**CH_4 Production (µmoles/g_{cat}/s) (x1000)**	**CO_2 Production (µmoles/g_{cat}/s) (x1000)**	**Reference**
20	18000	0.59	140	12	Subramanian *et al.*, 2010
14	15000	0.14	33	20	the present study
25	15000	0.19	44	30	
35	15000	0.31	47	38	

Results by (Subramanian *et al.*, 2010) indicate higher CO conversions accompanied by much higher methane production. It can be clearly seen that (Table 4.5) even the highest conversion achieved in this study on Rh-La/SiO_2 is half of the reported conversion value in literature.

Not many previous studies have been reported regarding the activation and deactivation behaviors of Rh- based catalysts in CO hydrogenation. It has been suggested that deactivation during the reaction may be due to the inhibiting effect of CO since strongly adsorbed CO on Rh sites may be less likely to be hydrogenated. The restructuring of the Rh surface during the reaction may also be a cause for the deactivation (Gao, 2009).

The catalytic activity in CO hydrogenation was reported for Rh/La_2O_3/SiO_2 catalyst, with lanthana loadings ranging from 0.1% to 8.5% (Kieffer *et al.*, 1988). It was shown by both characterization and activity tests that the metal particles were coated by lanthana, and as the amount of La deposited onto the Rh increased, a relative deactivation of the catalyst diminishing both the total CO conversion and the activity towards oxygenates is likely to be expected. Borer and Prins (1993) also reported that, for Rh–La/SiO_2 prepared by co- impregnation, the addition of a small amount of La can improve Rh dispersion leading to higher catalytic performance, but too high La_2O_3 loading is not desirable since La tends to cover Rh particles.

4.3.1. Effect of Temperature

Results of experiments conducted at 25 bar, demonstrating the dependence of CO conversion and product distribution on temperature, are presented in Figures 4.11-4.12. As elevated temperatures provide better catalytic activity but produce more carbon dioxide and methane, CO hydrogenation conducted at 300°C and 25 bar displayed higher CO conversion (8.4%) with 0.49 micromole/gcat/s CH_4 and 0.27 micromole/gcat/s CO_2 productions at steady state conditions (Figure 4.11). However, in accordance with the low CO conversion (2.5%), CO hydrogenation conducted at 270°C produced approximately ten times lower product than those shown in Figure 4.11. Raising the temperature to 285°C also improved methane and carbon dioxide productions significantly.

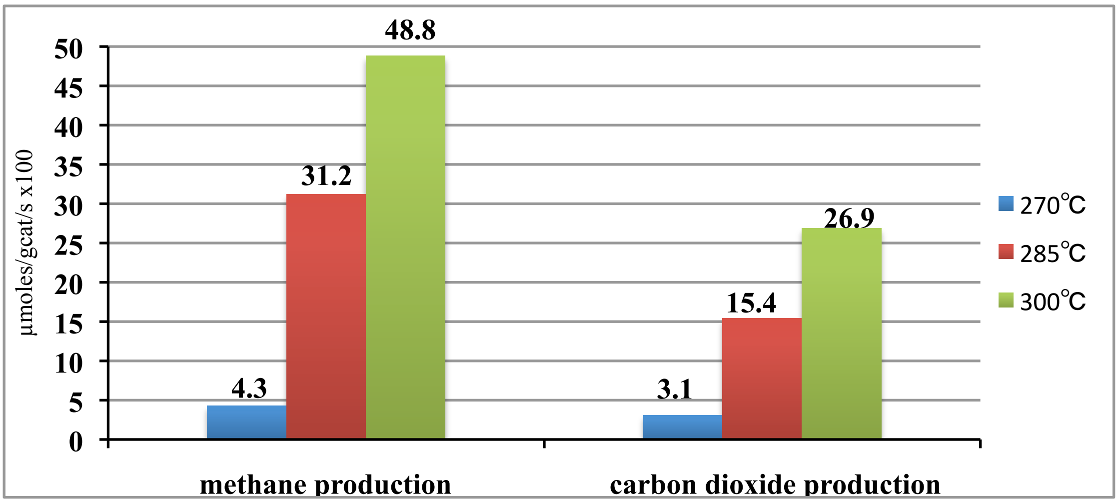


Figure 4.11. Comparison of CH_4 and CO_2 production over Rh-La/SiO_2 at different temperatures (Pressure at 25 bar).

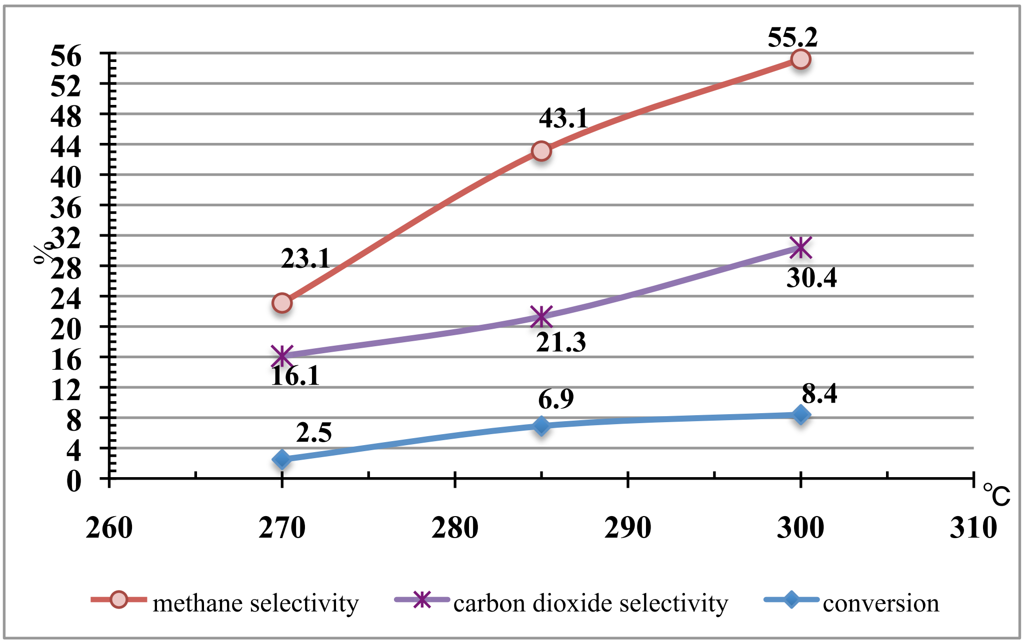


Figure 4.12. Effect of temperature on conversion and CH_4, CO_2 selectivity over Rh-La/SiO_2 at 25 bar.

As seen in Figure 4.29, at between 285°C and 300°C, methane selectivity climbed up to 43% and 55%, respectively. Similarly, an upward trend was observed in carbon dioxide selectivity with increasing reaction temperature. GC-MS chromatograms of experiments at three different temperatures are provided in Appendix B (Figure B.5).

Although singly promoted catalyst exhibited CO conversions lower than those over the Rh-La-V/SiO_2 catalyst, methane and carbon dioxide selectivity over Rh-La/SiO_2 were more or less in same range with doubly promoted catalyst (CH_4; 37-47%, CO_2; 18-26%).

4.3.2. Effect of Pressure

Results of experiments demonstrating the dependence of CO conversion and product distribution on the reaction pressure at 270°C are presented in Figures 4.13-4.14. GC-MS chromatograms of experiments at three different pressured are also provided in Appendix B (Figure B.6). The Rh-La/SiO_2 catalyst exhibited a steady state CO conversion level around 1.2% at 14 bar. When the pressure was increased to 35 bar, CO conversion reached approximately 4% as selectivity for CH_4 decreased from 23% to 15%. The selectivity for methane at 25 bar was almost same as that obtained at 14 bar. According to Figure 4.14, the lowest carbon dioxide (ca. 13%) and methane selectivities were (15%) was observed at 35 bar. Since CO conversions changed slightly with pressure, influence of pressure on formation of products was not remarkable (Figure 4.13).

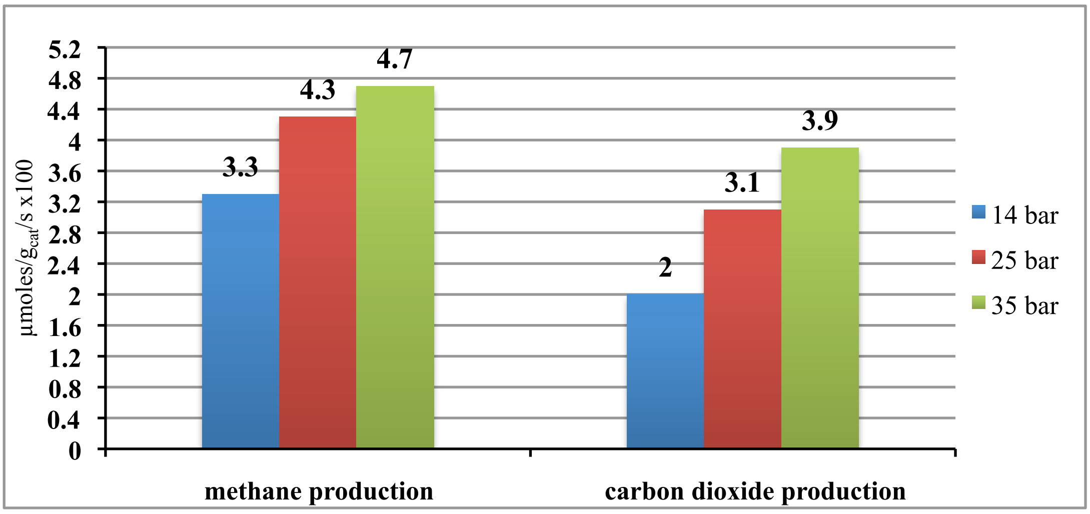


Figure 4.13. Comparison of CH_4 and CO_2 production over Rh-La/SiO_2 at different pressures (Temperature at 270^0C).

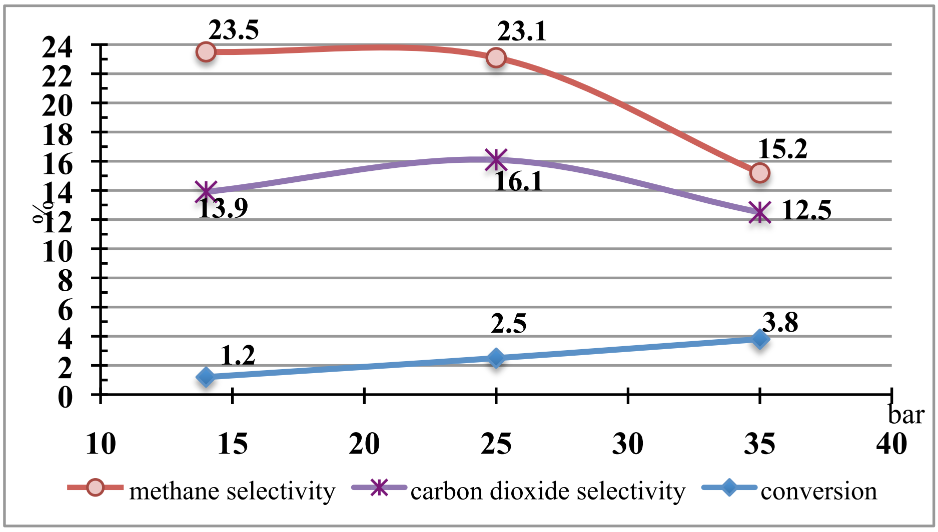


Figure 4.14. Effect of pressure on conversion and CH_4, CO_2 selectivity over Rh-La/SiO_2 at 270^0C.

4.4. Activity and Selectivity of the Rh-La-V/SiO_2 Catalyst

4.4.1. Effect of Reaction Temperature

The dependence of CO conversion and product distribution on reaction temperature was studied over the La-V promoted catalyst. The reduction temperature had a pronounced effect on the catalyst behavior. Kowalski *et al.* (1985) reported that a higher temperature of reduction for V-promoted Rh based catalysts (400 vs 200^oC) always produced less active but more selective catalysts. After the addition of La, V or Fe, higher reduction temperatures were required for the reduction of Rh. Regarding doubly and triply promoted Rh/SiO_2 catalysts, the addition of a second promoter or a third promoter hindered the reduction of Rh. La was not reduced at temperatures below 500°C (Mo et al, 2009b). Therefore, the Rh-La-V/SiO_2 catalyst prepared in this study was reduced *in situ* under hydrogen flow for 2 hours at 500°C prior to each reaction test.

The composition of the feed gas mixture was 10 mol per cent CO, 20 mol per cent H_2 and balance N_2 in the 50 cm^3/min total inlet flow rate. Reactions were carried out at 240^oC, 270^oC and 300^oC at three different pressures, namely 14, 25 and 35 bar using a fixed contact time of 0.98 $mg.min.\mu mol^{-1}$. Three additional reaction tests were conducted to observe effect of temperature at 255^oC, 285^oC and 315^oC at a reaction pressure of 25 bar.

Subramanian and coworkers (2010) also examined the effect of reaction temperature over La and V promoted Rh/SiO_2 for ethanol synthesis by CO hydrogenation at 20 bar. It was concluded that methanation must be kinetically limited in order to increase the ethanol yield and selectivity, because methane is the thermodynamically favored product at all temperatures. In order to avoid the undesirable methane product, CO hydrogenation over Rh-based catalysts for alcohol production is preferably conducted at temperatures below 300°C (Mei *et al.*, 2010).

In general, CO conversion and methane selectivity levels observed in reaction tests increased with temperature, as would be expected. Experimental results indicated that increasing the temperature from 240 to 300^oC favored methane formation and selectivity.

The selectivity to methane approached nearly 60% at the temperature of 300°C. Results obtained at steady state conditions are reported in Tables 4.6-4.11 and Figures 4.15-4.21.

4.4.1.1. Experiments at 14 bar. The Rh-La-V/SiO_2 catalyst exhibited a CO conversion of approximately 3% at 240°C at steady state. When the temperature was increased to 270°C, CO conversion reached about 6.6% and selectivity for CH_4 increased slightly. According to results presented in Tables 4.6-4.7 and Figures 4.15-4.16, the highest CO conversion obtained was 23% accompanied by a methane selectivity of 35.7% at steady state.

Table 4.6. Effect of temperature on the performance of Rh-La-V/SiO_2 at 14 bar.

Temperature (^{0}C)	**CO conversion (%)**	**CH_4 Production (µmoles/gcat/s) (x100)**	**CO_2 Production (µmoles/g_{cat}/s) (x100)**	**CH_4 Selectivity (%)**	**CO_2 Selectivity (%)**
240	2.7	8.8	7.2	28.4	23.2
270	6.6	22.6	9.9	30.2	12.8
300	23.0	92.1	43.3	35.7	16.8

Table 4.7. Effect of temperature on ethanol production over Rh-La-V/SiO_2 at 14 bar.

Temperature (^{0}C)	**240**	**270**	**300**
C_2H_5OH Production (µmoles/g_{cat}/s) (x1000)	3.1	1.8	1.9

Subramanian *et al.* (2010) investigated CO hydrogenation over 1.5 wt% Rh/SiO_2 promoted with La and V oxides. Ethanol selectivity reached 51.8% (close to the highest literature value) at a CO conversion of 7.9%, achieved along with a corresponding methane selectivity of 15.4% at 270°C, 14 bar and H_2/CO ratio of 2. Although the CO conversion obtained in the present work was close to 7.9%, formation of CH_4 and C_2-C_4 alkanes seem to suppress the formation of oxygenated products. In contradiction to the result reported by Subramanian *et al.*, only trace amounts of ethanol were obtained over the Rh-La-V/SiO_2

catalyst at 14 bar (Table 4.7), and ethanol produced at 240°C was only slightly higher.

There was no dramatic change in CO_2 production between 240°C and 270°C. As regards CO_2 selectivity, the lowest selectivity exhibited on the Rh-La-V/SiO_2 catalyst was ca. 13% at 270°C. The amounts of CH_4 and CO_2 produced are so low that they were multiplied by 100 in order to illustrate the trends in Figure 4.16.

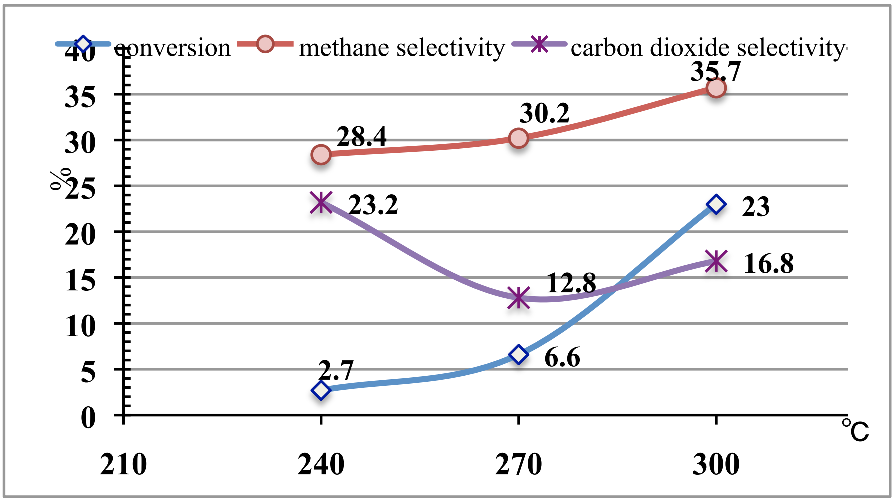


Figure 4.15. Effect of temperature on CO conversion and CH_4 and CO_2 selectivity over Rh-La-V/SiO_2 at 14 bar.

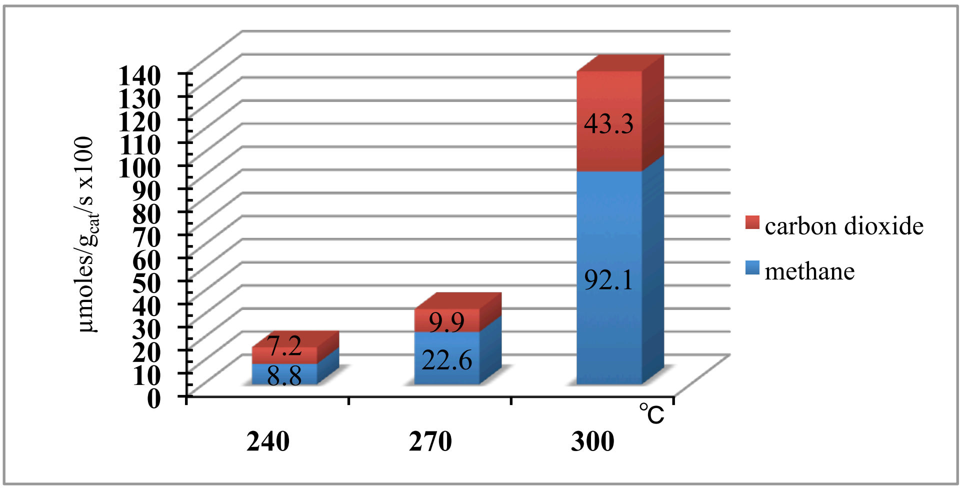


Figure 4.16. Comparison of CH_4 and CO_2 production over Rh-La-V/SiO_2 at different temperatures (Pressure at 14 bar).

In addition to methane, C_2-C_4 hydrocarbons were principal products under these conditions. The other products detected in trace amounts were methanol, dimethyl ether, acetaldehyde, acetic acid and ethyl ether. Small amounts of pentane and hexane were also detected at higher temperatures. It was observed that low temperatures favored olefinic hydrocarbons such as ethylene, propylene and butene. For example, the ratio of the peak area under propylene to propane was higher at 240°C in comparison with ratios calculated at the other two temperatures. Increasing the temperature resulted in the formation of some alkanes such as propane and butane. The representative GC-MS chromatograms given in Appendix B (Figure B.1) are used in making these comments. The chromatograms given demonstrate products other than methane, carbon dioxide, ethane, ethylene and water.

4.4.1.2. Experiments at 25 bar. Methane, carbon dioxide and ethanol productions were calculated for six different temperatures, using peaks obtained in GC-MS chromatograms, and the results are shown in Table 4.8 and Table 4.9. Regarding these tables, to provide better vision production amounts and selectivity are plotted in Figures 4.17-4.19.

Table 4.8. Effect of temperature on the performance of Rh-La-V/SiO_2 at 25 bar.

Temperature (^{0}C)	**CO conversion (%)**	**CH_4 Production (µmoles/g_{cat}/s) (x100)**	**CO_2 Production (µmoles/g_{cat}/s) (x100)**	**CH_4 Selectivity (%)**	**CO_2 Selectivity (%)**
240	2.8	5.8	5.2	19.4	17.4
255	7.5	24.6	11.7	31.2	14.8
270	9.1	37.9	18.3	36.5	17.7
285	17.9	75.8	31.9	40.4	17.0
300	29.4	143.3	81.7	46.4	26.4
315	32.6	185.8	96.3	54.2	28.1

Table 4.9. Effect of temperature on ethanol production over Rh-La-V/SiO_2 at 25 bar.

Temperature (^0C)	**C_2H_5OH Production (μmoles/gcat/s) (x1000)**	**C_2H_5OH Selectivity (%)**
240	7.6	5.1
255	22.3	5.5
270	59.1	8.7
285	77.4	8.3
300	63.7	4.1
315	70.6	3.9

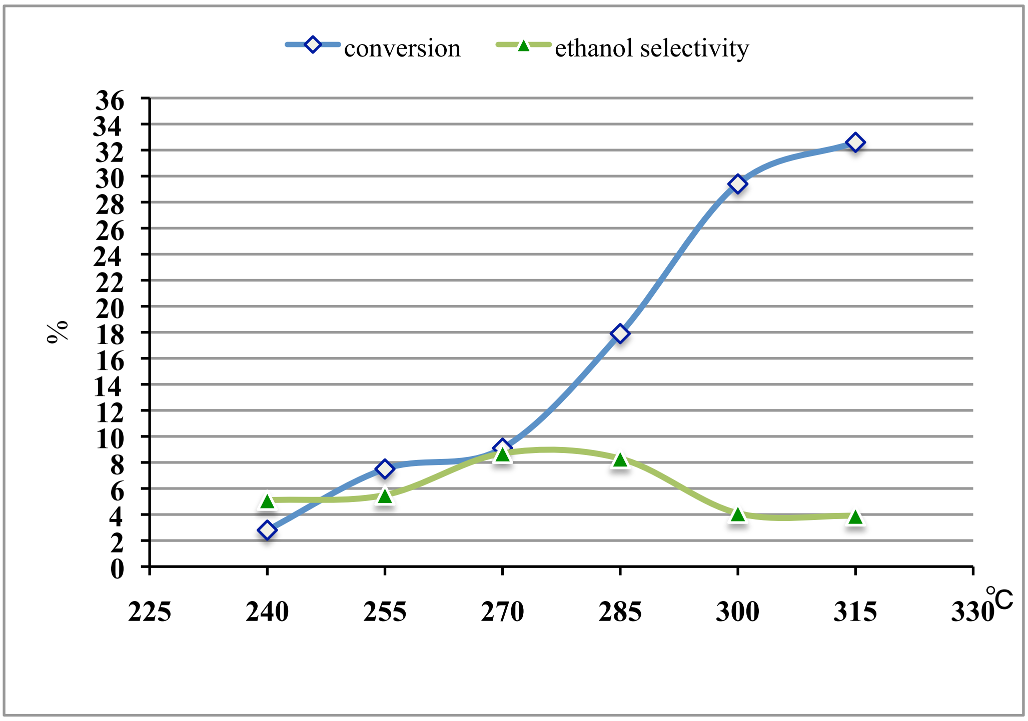


Figure 4.17. Effect of temperature on CO conversion and C_2H_5OH selectivity over Rh-La-V/SiO_2 at 25 bar.

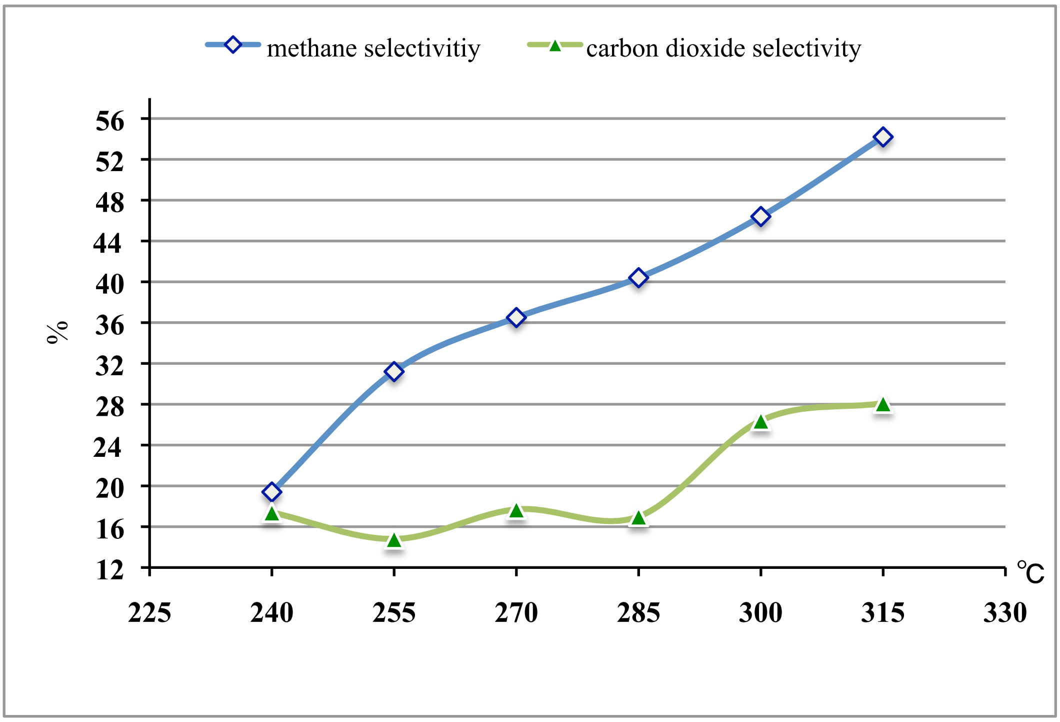


Figure 4.18. Effect of temperature on CH_4 and CO_2 selectivity over Rh-La-V/SiO_2 at 25 bar.

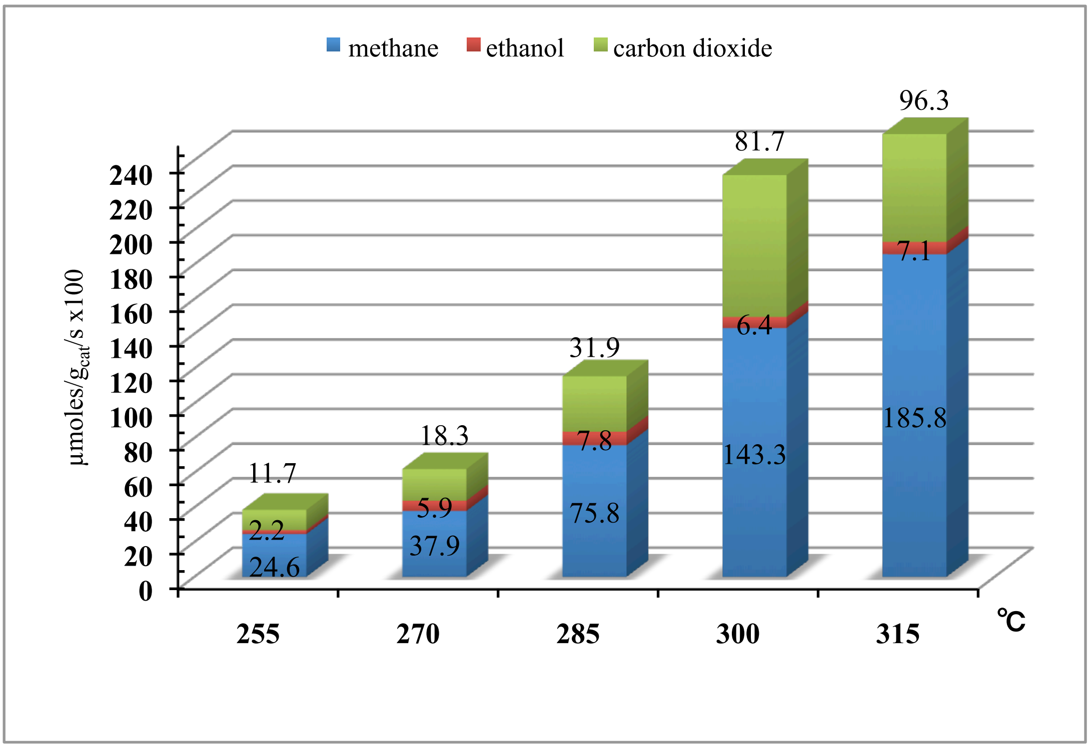


Figure 4.19. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different temperatures (Pressure at 25 bar).

The experimental results reported in Table 4.8 and Figure 4.17, show that the steady state CO conversion was around 3% and 33% at 240°C and 315°C, respectively. A rapid increase was observed in CO conversion rates as the temperature was raised above 270°C.

Raising the reaction temperature from 240°C to 315°C boosted up CH_4 selectivity significantly. Figure 4.18 shows that methane selectivity increased from around 19% to 54% at 240°C and 315°C, respectively. On the other hand, CO_2 selectivity was less affected by increasing temperature up to 285°C. Further increase in temperature resulted in a higher CO_2 selectivity of around 28%. CH_4 and CO_2 productions at 240°C were 0.058 and 0.052 micromole/g_{cat}/s, respectively. Figure 4.19 shows relative production rates of methane, carbon dioxide and ethanol. In the temperature range of 255-315°C, the methane produced by the catalyst is twice as much compared to carbon dioxide.

Ethanol production and selectivity over the 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalyst are given in Table 4.9. Ethanol poduction increased with temperature up to 285^{o}C. Further increment of temperature did not favor formation of ethanol. Regarding selectivity to ethanol, the highest selectivity obtained at 270^{o}C was 8.7% accompanied by a methane selectivity of 36.5%. This is followed by 8.2% ethanol selectivity at 285^{o}C (Figure 4.17). It can be inferred that formation of ethanol is favored in the range of 270-285^{o}C, as also illustrated by Figure 4.15. Hu and coworkers (2007) investigated the effect of temperature over Mn-Rh/SiO_2 catalyst for CO hydrogenation in a microchannel reactor. They have also noted that alcohol synthesis over Rh-Mn/SiO_2 is favorable at temperatures lower than 280^{0}C since at higher temperatures ethanol selectivity decreases remarkably while methane selectivity increases.

Methane, C_2-C_4 alkanes, ethanol, acetic acid and ethyl ether were found to be the major products although product distrubition changed slightly at different temperatures. For instance, significant amount of pentane was produced at 315^{0}C whereas trace amount of pentane was detected at 240^{0}C. Similarly, a higher peak area was measured for ethyl ether at 285^{0}C in comparison with the ethyl ether peaks at 255^{0}C and 315^{0}C. The largest peak area for acetic acid was observed at 255^{0}C and it diminished gradually at higher temperatures. Other minor co-products were dimethyl ether, acetaldehyde and methanol.

Trace amount of acetone was also detected at 315^0C. Formation of olefinic hydrocarbons such as ethylene, propylene and butene was comparable to that of alkanes at temperatures below 270^0C. The ratio of peak areas under propylene to propane was remarkably higher at 255°C in comparison with 270^0C. Smaller peaks were observed for olefinic products at increasing temperatures in spite of higher CO conversions. High temperatures gave rise to the formation of alkanes such as propane, butane and pentane. The GC-MS chromatograms that show product distrubitions at 255°C 285°C and 315°C are given in Appendix B (Figure B.2). The products other than methane, carbon dioxide, ethane, ethylene and water are also shown in the range of the chromatograms given.

4.4.1.3. Experiments at 35 bar. The CO conversions attained at steady state conditions were around 6.5% and 31% at 240°C and 300°C, respectively (Table 4.10 and Figure 4.20). As reaction temperature was raised from 240°C to 270°C, CO conversion increased slightly from 6.5% to ca. 9%. Raising reaction temperature from 240 to 300°C increased the selectivity to methane from about 38 to 60% whereas carbon dioxide selectivity remained unaffected around 23%. There was no dramatic difference between methane selectivities at 270°C and 300°C. In comparison with results of the experiment performed at 300°C, both carbon dioxide and methane selectivity were slightly higher at 270°C, as also seen in Figure 4.20.

Table 4.10. Effect of temperature on the performance of Rh-La-V/SiO_2 at 35 bar.

Temperature (^{0}C)	**CO conversion (%)**	**CH_4 Production (µmoles/gcat/s) (x100)**	**CO_2 Production (µmoles/gcat/s) (x100)**	**CH_4 Selectivity (%)**	**CO_2 Selectivity (%)**
240	6.5	24.6	14.5	38.3	22.7
270	8.9	56.7	27.1	60.4	28.9
300	30.6	176.5	72.1	58.1	23.7

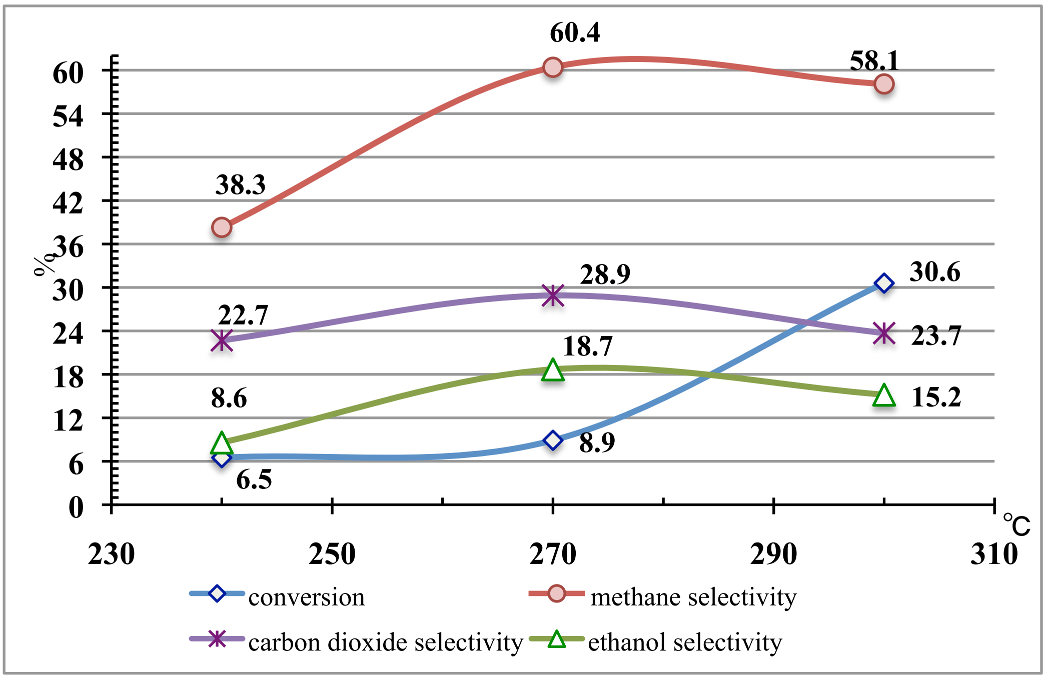


Figure 4.20. Effect of temperature on conversion and CH_4, C_2H_5OH, CO_2 selectivity over Rh-La-V/SiO_2 at 35 bar.

The amount of methane produced was higher than those of carbon dioxide and ethanol at all temperatures (Figure 4.21). The changes in ethanol selectivity and production rates over 1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2 catalyst are given in Table 4.11. Ethanol poduction rates were 0.028 and 0.23 micromole/g_{cat}/s at 240°C and 300°C, respectively.

Table 4.11. Effect of temperature on ethanol production over Rh-La-V/SiO_2 at 35 bar.

Temperature (^{0}C)	**C_2H_5OH Production (µmoles/gcat/s) (x1000)**	**C_2H_5OH Selectivity (%)**
240	27.6	8.6
270	85.2	18.7
300	228.6	15.2

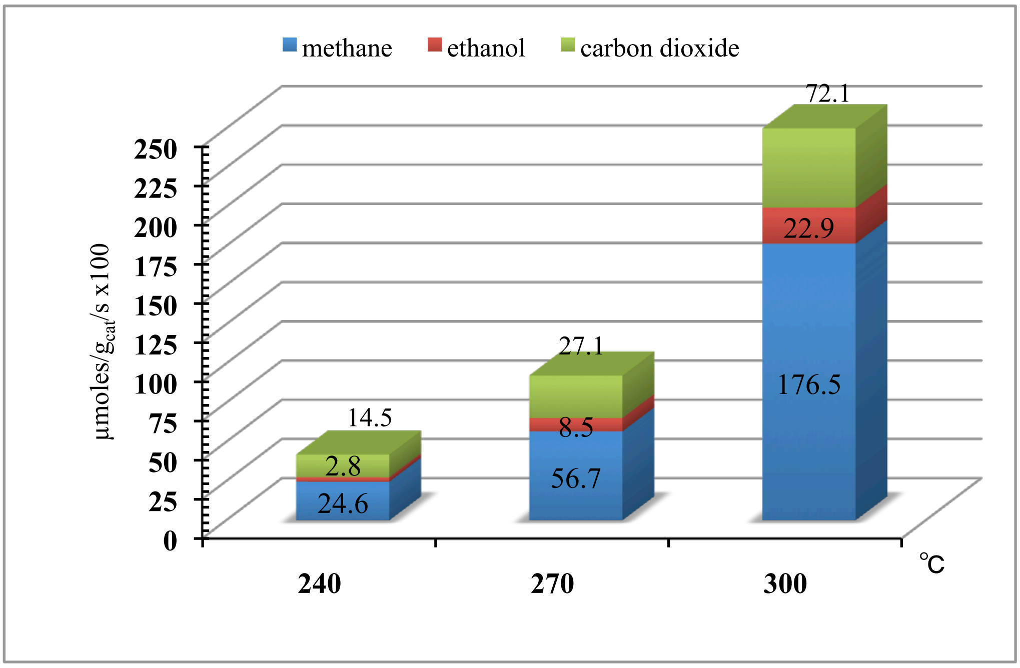


Figure 4.21. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different temperatures (Pressure at 35 bar).

Regarding selectivity to ethanol, the highest selectivity obtained was around 19% with a production rate of 0.085 micromole/g_{cat}/s at 270°C. The next best result is 15.2% ethanol selectivity at a production rate of 0.23 micromole/g_{cat}/s at 300°C (Table 4.11). Luo *et al.* (2001) tested a series of Sm and V promoted Rh/SiO_2 catalysts for investigating the activity and selectivity to C_2 oxygenates. The reactions were carried out at 280°C and 30 bar. Ethanol selectivity achieved was about 30% at a CO conversion of 5%. It was also stated that the ethanol selectivities on vanadium containing Rh catalysts were much higher than those of acetic acid and acetaldehyde. The yield of ethanol attained in the present study at 35 bar and 270°C is close to results reported by Luo and coworkers.

In addition to methane, C_2-C_4 alkanes, ethanol, acetic acid and ethy ether were major products. Small amounts of C_2-C_4 alkenes, pentane and hexane were also detected. The other products observed were trace amounts of methanol, dimethyl ether and acetaldehyde. In general, low temperatures favored olefinic hydrocarbons such as ethylene, propylene and butene. Increasing the temperature up to 300^0C led to the formation of pentane in additon to enhancing the formation of propane and butane. The peak area for acetic acid was almost the same size as that of ethanol at 270^0C. When the temperature was changed to 240^0C, a higher peak area appeared for acetic acid in comparison with the ethanol peak. The difference between peak areas of acetic acid and ethanol was significantly higher at 300^0C (in favor of ethanol). It can be inferred that increasing temperature enhanced formation of ethanol more than that of acetic acid. The GC-MS chromatograms that show product distrubition at 35 bar are given in Appendix B (Figure B.3).

4.4.2. Effect of Reaction Pressure

Results of experiments demonstrating the dependence of CO conversion and product distribution on the reaction pressure are presented in Tables 4.12-4.15 for the Rh-La-V/SiO_2 catalyst. Ethanol production and selectivity for various products are also plotted in Figures 4.22-4.27. The effect of pressure was examined in experiments performed at 240°C, 270°C and 300°C using a fixed contact time of 0.98 mg.min.μmol^{-1}.

The influence of pressure on CO conversion was insignificant compared to the influence of temperature. In the literature, there is no consensus regarding the effect of pressure on product selectivity for CO hydrogenation. Increasing pressure increases the equilibrium concentration of ethanol in CO hydrogenation. However, Subramanian *et al.* (2010) reported that ethanol selectivity was higher at 14 bar than at 40 bar whereas the rate of CO conversion increased with pressure, consistent with results of Hu *et al.* (2007). The selectivity to methane was greater at 40 bar compared to 14 bar, while ethanol selectivity decreased at 40 bar. On the other hand, Hu *et al.* (2007) reported that increasing the pressure reduced methane selectivity while increasing the selectivity to oxygenates and CO conversion over Rh–Mn–V/SiO_2 catalyst at 270°C. In another study, CO conversion over cerium promoted Rh/SiO_2 decreased slightly when pressure was changed from 20 bar to 50 bar at 280^0C. Besides, the selectivity to methane was reported higher at 50 bar (Kiennemann *et al.*, 1987). In the present study, increasing pressure from 14 bar to 35 bar resulted in higher selectivity with enhanced production rates for both methane and ethanol. Also, higher amount of carbon dioxide was produced at 35 bar in comparison to lower pressures.

4.4.2.1. Experiments at 240^0C. The Rh-La-V/SiO_2 catalyst exhibited CO conversion levels of approximately 3% at 14 bar and 25 bar under steady state conditions. When the pressure was increased to 35 bar, the CO conversion reached was around 6.5%, and the selectivity for CH_4 reached 38%. The selectivities for carbon dioxide at 14 and 35 bar were almost same at around 23%. According to results presented in Table 4.12 and Figure 4.22, the lowest methane selectivity obtained was ca. 19% and carbon dioxide selectivity was 17% at 25 bar. It is worth noting that the amounts of methane and carbon dioxide obtained at 25 bar were lower than those at 14 bar. However, ethanol production was improved at 25 bar in spite of the same total CO conversion, as also observed in Figure 4.23. The ratio of CO_2 to CH_4 production rates was close to unity at 14 and 25 bar. On the other hand, more methane appeared relative to carbon dioxide formed at 35 bar.

Table 4.12. Effect of pressure on the performance of Rh-La-V/SiO_2 at 240^0C.

Pressure (bar)	**14**	**25**	**35**
CO conversion (%)	2.7	2.8	6.5
CH_4 Production (μmoles/g_{cat}/s) (x100)	8.8	5.8	24.6
CO_2Production (μmoles/g_{cat}/s) (x100)	7.2	5.2	14.5
C_2H_5OH Production (μmoles/g_{cat}/s) (x1000)	3.1	7.6	27.6
CH_4 Selectivity (%)	28.4	19.4	38.3
C_2H_5OH Selectivity (%)	--	5.1	8.6
CO_2 Selectivity (%)	23.2	17.4	22.7

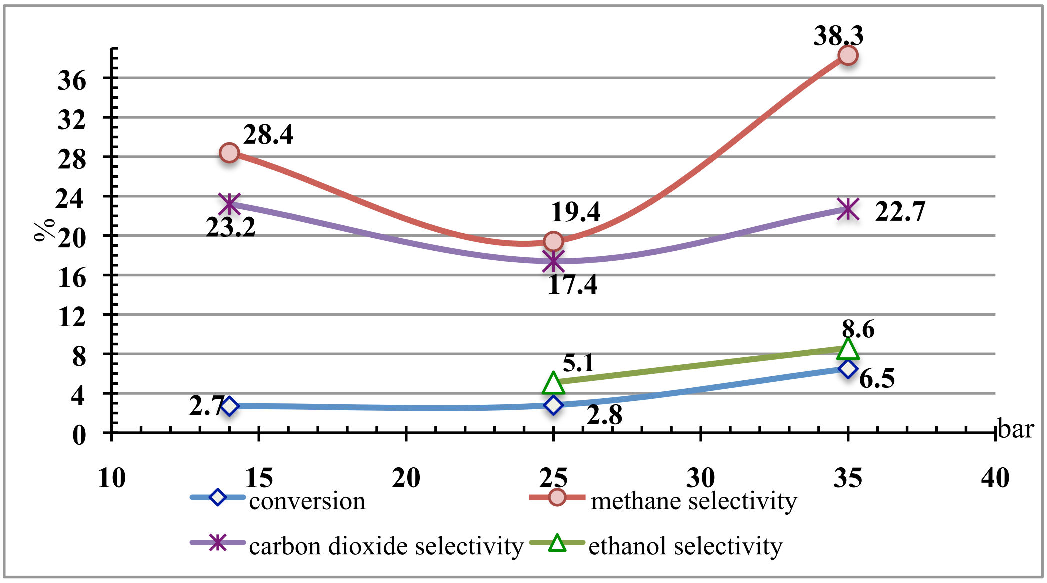


Figure 4.22. Effect of pressure on conversion and CH_4, C_2H_5OH, CO_2 selectivity over Rh-La-V/SiO_2 at 240^0C.

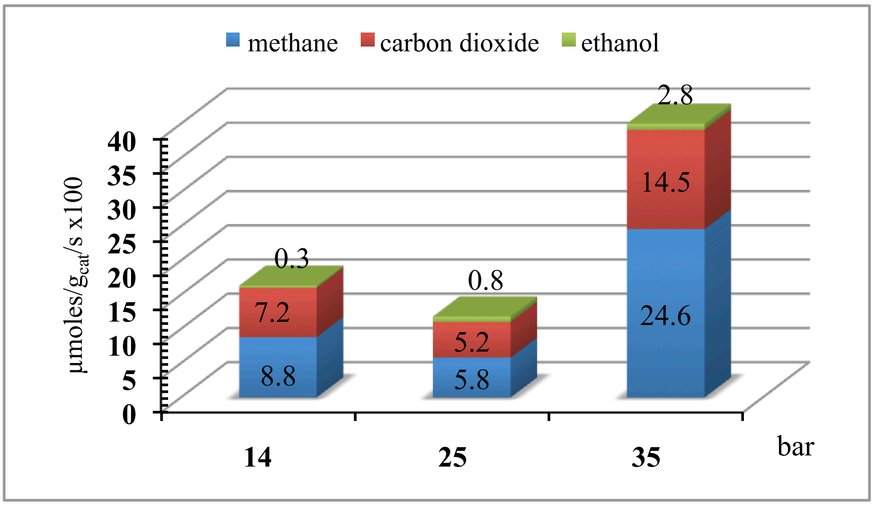


Figure 4.23. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different pressures (Temperature at 240^0C).

During the reaction conducted at 14 bar, ethanol production observed was in quite low amounts (Figure 4.23). There was no striking change in ethanol selectivity considering results given in Table 4.9 at 25 and 35 bar. Ethanol production rates increased with pressure, and the highest selectivity obtained was 8.6% at 35 bar. It can be inferred that higher pressures enhanced the formation of ethanol.

4.4.2.2. Experiments at 270^{0}C. When pressure was changed from 14 to 25 bar, higher CO conversion was attained with 0.038 micromole/g_{cat}/s CH_4 and 0.018 micromole/g_{cat}/s CO_2 production rates at steady state conditions (Table 4.13 and Figure 4.24). However, further increse in pressure did not enhance CO conversion which remained around 9%. The formation of methane and carbon dioxide increased when pressure was elevated.

Table 4.13. Effect of pressure on the performance of Rh-La-V/SiO_2 at 270^{0}C.

Pressure	**14**	**25**	**35**
CO conversion (%)	6.6	9.1	8.9
CH_4 Production (µmoles/g_{cat}/s) (x100)	22.6	37.9	56.7
CO_2Production (µmoles/g_{cat}/s) (x100)	9.9	18.3	27.1
C_2H_5OH Production (µmoles/g_{cat}/s) (x1000)	--	59.1	85.2
CH_4 Selectivity (%)	30.2	36.5	60.4
C_2H_5OH Selectivity (%)	--	8.7	18.7
CO_2 Selectivity (%)	12.8	17.7	28.9

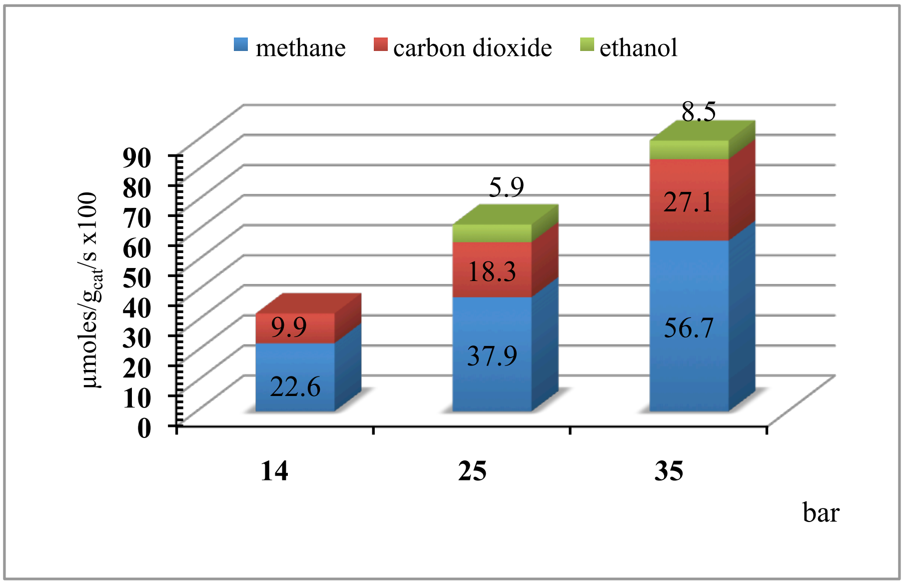


Figure 4.24. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different pressures (Temperature at 270^{0}C).

Figure 4.25 shows the change in selectivity and conversion with respect to pressure. Raising the pressure from 14 to 35 bar increased the selectivity to methane from about 30 to 60% while carbon dioxide selectivity reached 29% at 35 bar. Results in Table 4.13 and Figure 4.25 indicate that the methane selectivity obtained at 25 bar was ca. 37%.

Ethanol poduction rate increased with pressure, and the highest selectivity obtained at 35 bar was 18.7%. Steady state ethanol poduction rates were around 0.06 and 0.09 micromole/g_{cat}/s at 25 bar and 35 bar, respectively.

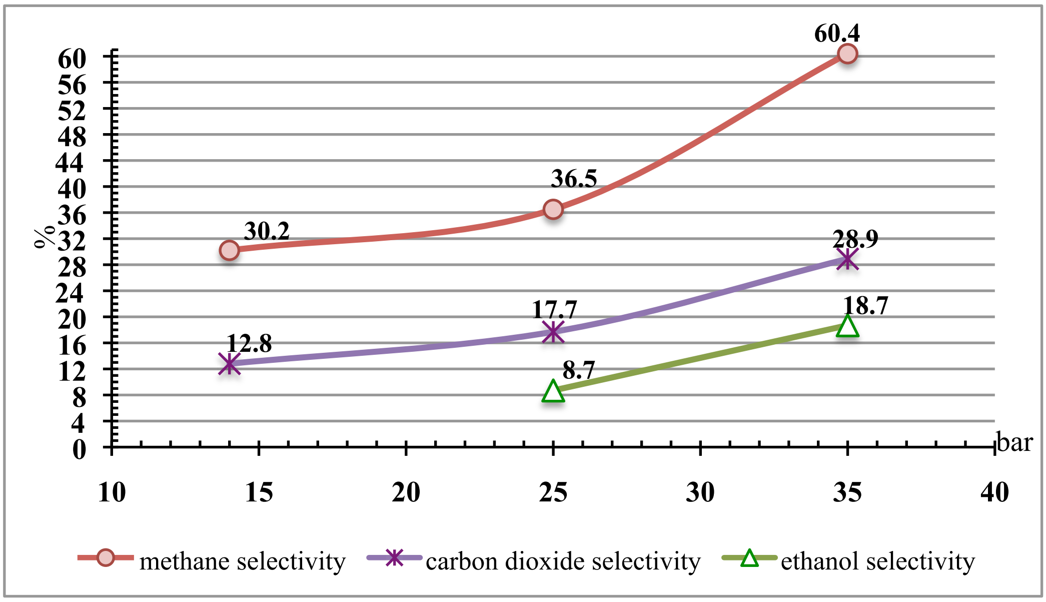


Figure 4.25. Effect of pressure on CH_4, C_2H_5OH and CO_2 selectivity over Rh-La-V/SiO_2 at 270^0C.

<u>4.4.2.3. Experiments at 300^0C.</u> According to the results presented in Table 4.14 and Figure 4.26, the lowest CO conversion obtained was 23% with methane selectivity of around 36% at 14 bar. The catalyst exhibited a CO conversion level of approximately 29% at 25 bar. At 35 bar, on the other hand, about 31% CO conversion was obtained along with a CH_4 selectivity of 58%.

Table 4.14. Effect of pressure on the performance of Rh-La-V/SiO_2 at 300^0C.

Pressure	**14**	**25**	**35**
CO conversion (%)	23.0	29.4	30.6
CH_4 Production (µmoles/g_{cat}/s) (x100)	92.1	143.3	176.5
CO_2 Production (µmoles/g_{cat}/s) (x100)	43.3	81.7	72.1
C_2H_5OH Production (µmoles/g_{cat}/s) (x1000)	--	63.7	228.6
CH_4 Selectivity (%)	35.7	46.4	58.1
C_2H_5OH Selectivity (%)	--	4.1	15.2
CO_2 Selectivity (%)	16.8	26.4	23.7

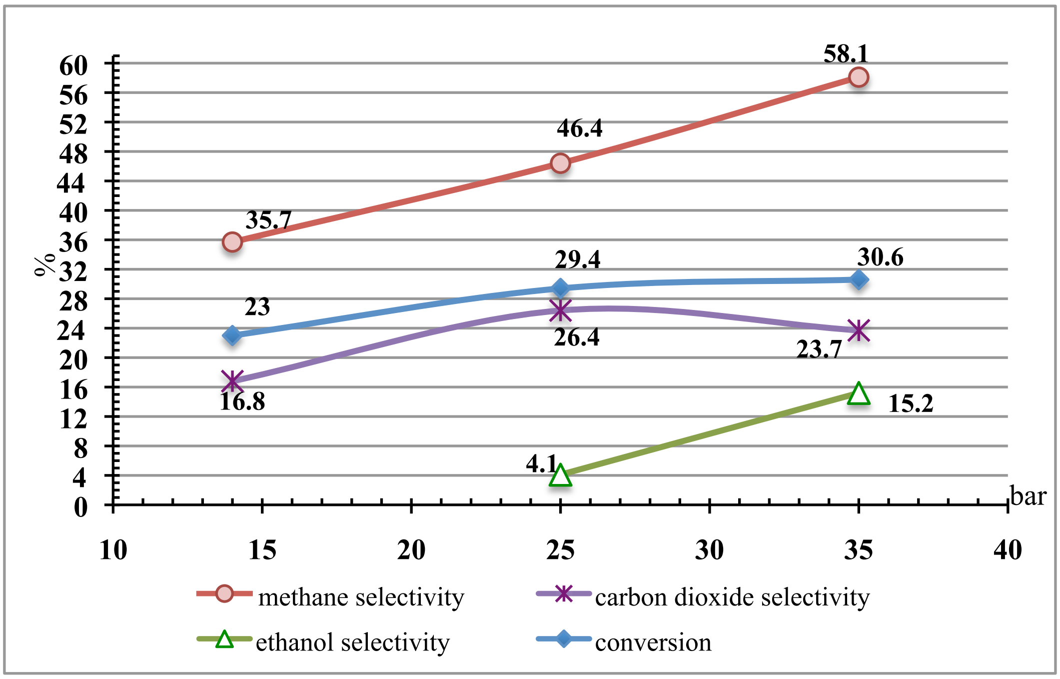


Figure 4.26. Effect of pressure on conversion and CH_4, C_2H_5OH, CO_2 selectivity over Rh-La-V/SiO_2 at 300^0C.

The formation rates of methane and ethanol were improved as the pressure increased. However, as shown in Figure 4.27, CO_2 production rate was somewhat reduced as pressure was increased from 25 bar to 35 bar. The corresponding carbon dioxide selectivities were 26% and 24% at 25 bar and 35 bar, respectively.

Ethanol production rate increased with pressure, and ethanol selectivity reached at 35 bar was 15% while only 4% selectivity was achieved at 25 bar. The steady state ethanol production rates were 0.064 and 0.23 micromole/g_{cat}/s at 25 and 35 bar, respectively.

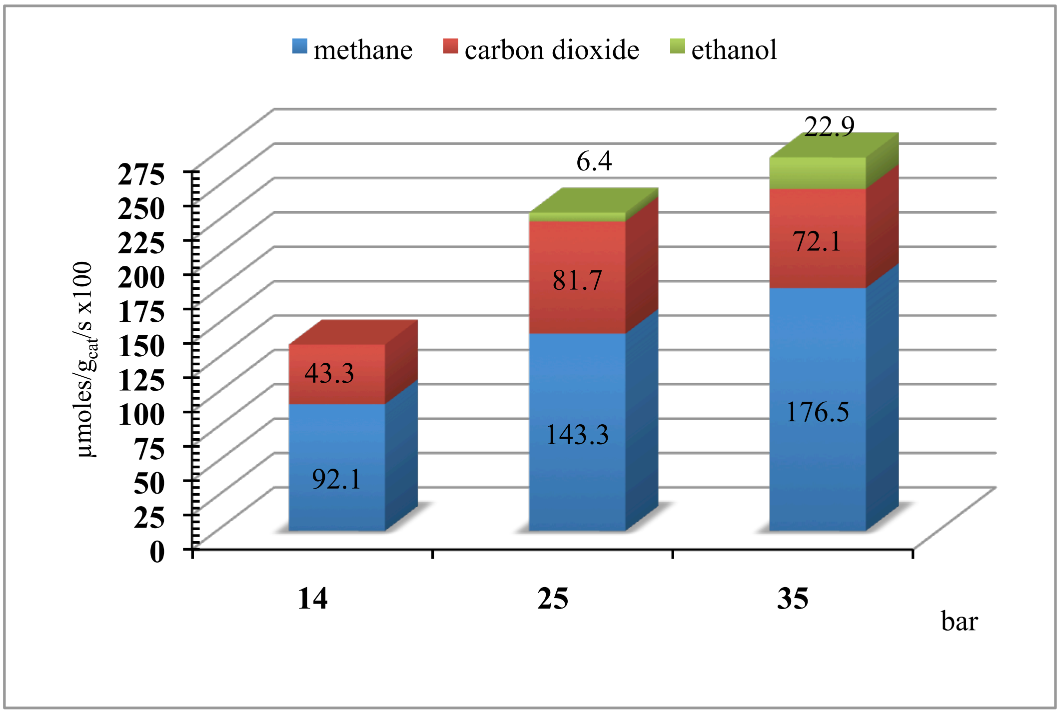


Figure 4.27. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different pressures (Temperature at 300^0C).

4.4.3. Selectivity to ethanol and methane at different temperature-pressure values

In order to demonstrate the influences of both temperature and pressure more clearly, the results of the experiments carried out at 25 bar and 35 bar were plotted in Figure 4.28 and Figure 4.29, which display both ethanol and methane selectivity with respect to CO conversions at different reaction conditions.

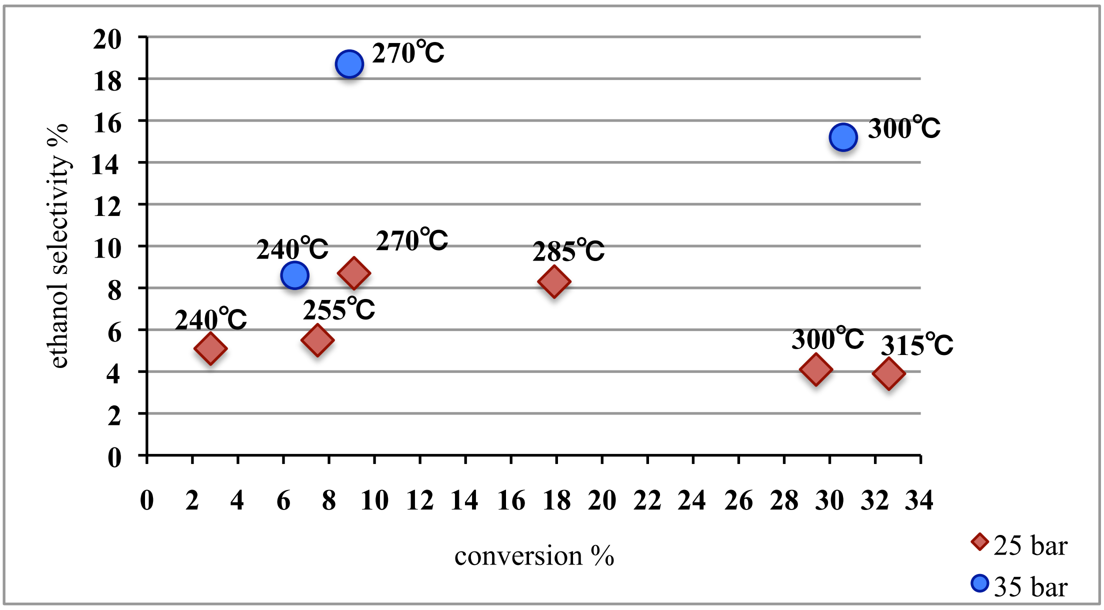


Figure 4.28. CO conversion and C_2H_5OH selectivity over Rh-La-V/SiO_2 at different temperatures and pressures

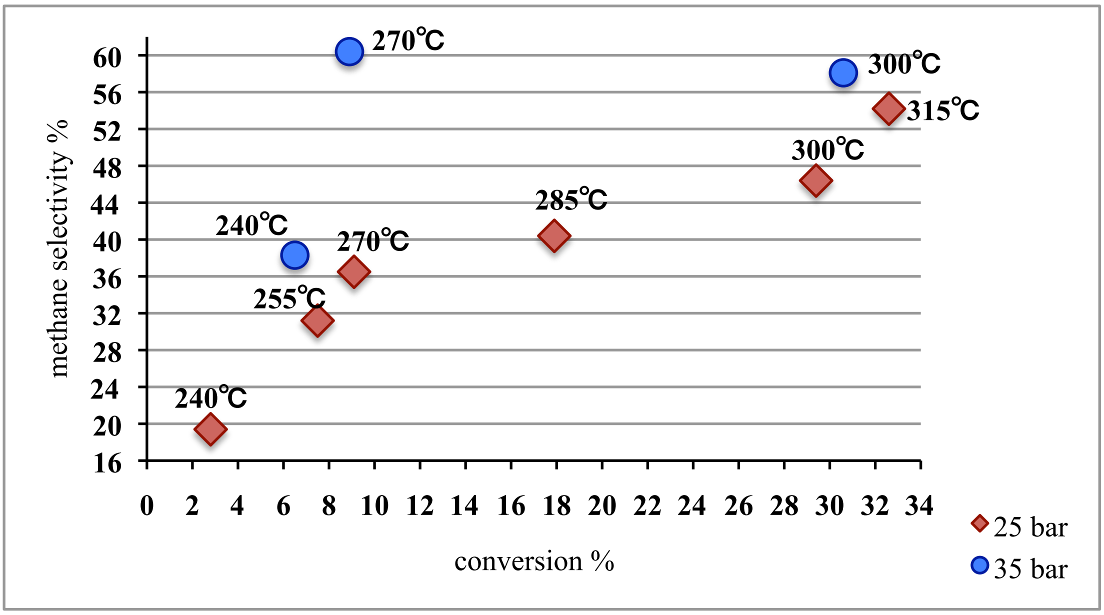


Figure 4.29. CO conversion and CH_4 selectivity over Rh-La-V/SiO_2 at different temperatures and pressures.

The influence of pressure on the activity and selectivity of CO hydrogenation for the production of oxygenates was reported to be insignificant compared to the influence of temperature (Haider *et al.*, 2009). Egbebi (2008) stated that the equilibrium concentration of ethanol in CO hydrogenation is favored by increasing pressures although this effect weakens at higher pressures in a logarithmic fashion.

Temperature is the key adjustable variable for overall CO conversion in the CO hydrogenation reaction. It is important to determine its effect on the selectivity to ethanol versus methane. Figure 4.24 clearly indicates that the maximum ethanol selectivity of 19% is obtained at 25 bar and 270^0C at around 9% CO conversion. However, CO conversion is almost doubled at 285°C with only a slight decrease in ethanol selectivity. Therefore the optimum temperature favoring ethanol production was selected as 285°C in experiments performed at 25 bar. On the other hand, higher pressure resulted in improved selectivity to ethanol at 270°C although the catalyst gave the same CO conversion at both pressures. Increasing the temperature up to 300°C at 35 bar led to much a higher CO conversion of ca 31%, with an ethanol selectivity around 15%. The best temperature alternative seems to be 300°C among experiments conducted at 35 bar.

Regarding methane, it is seen in Figure 4.29 that its selectivity increased rapidly as temperature was varied in the 240-270°C range in experiments at 25 bar, but further increases in temperature caused only moderate changes in methane selectivity. On the contrary, at 35 bar, methane selectivity stayed at same level as temperature was increased from 270 to 300°C. It can be concluded that temperatures between 270-300°C at higher pressure (35 bar) favored ethanol formation with methane selectivity varying in the range of 40-60%.

The selectivity levels for methane obtained over the Rh-La-V/SiO_2 catalyst are more or less similar to results reported in literature while the highest ethanol selectivity level attained in this study is noticeably lower. For example, the Rh–Mn/SiO_2 catalyst at 300°C and 54 bar exhibited about 40% CO conversion, with an ethanol selectivity of about 44%. Increasing the reaction temperature from 280 to 300°C increased CO conversion from about 25 to 40%, but the selectivity to methane also increased to 48%. It was noted that reaction temperature, rather than reaction pressure, has a strong influence on the product selectivity (Hu *et al.*, 2007). Haider and coworkers (2009) explored the influences of Fe promoter loading on the activity and selectivity of Rh-based catalysts for the direct synthesis of ethanol from syngas. Although the influence of pressure was moderate over

2wt%Rh–2.5wt%Fe/TiO_2, higher temperatures increased methane production at the expense of ethanol and methanol. Reaction conditions of 270^0C and 20 bar gave CO conversion and ethanol selectivity of around 12% and 28%, respectively.

4.4.4. Effect of W/F_{CO} Ratio

The effect of residence time (as measured by the W/F_{CO} ratio) on CO conversion was studied over the Rh-La-V/SiO_2 catalyst. Reaction tests were carried out at 285°C and 25 bar using a feed gas mixture of 10 mol per cent CO and 20 mol per cent H_2 (except one test conducted with feed of 20 mol per cent CO and 40 mol per cent H_2) with N_2 as balance. All gas flow rates were calculated at NTP (25°C and 1 atm). The weights of catalyst samples were 200, 250 and 400 mg but the total feed flow rates directly affecting contact time were also varied between 40 and 50 $cm^3.min^{-1}$. CO conversions reached at different W/F_{CO} ratios are presented in Table 4.15, while the influence of residence time on product selectivity is shown in Table 4.16 and Figure 4.30.

Table 4.15. Effect of W/F_{CO} ratio on the performance of Rh-La-V/SiO_2 (285°C, 25 bar).

W/F_{CO} ($mg.min.\mu mol^{-1}$)	**CO conversion (%)**	**CH_4 Production (µmoles/gcat/s) (x1000)**	**C_2H_5OH Production (µmoles/g_{cat}/s) (x1000)**	**CO_2 Production (µmoles/g_{cat}/s) (x1000)**
1.95	23.9	979.2	169.5	525.0
1.53	22.5	858.3	87.3	404.2
0.98	17.9	758	77.4	319.0
0.49	9.6	--	--	--

Table 4.16. Effect of W/F_{CO} ratio on selectivity of products over Rh-La-V/SiO_2 (285°C, 25 bar).

Space velocity ($cm^3/h/g_{cat}$)	**W/F_{CO} ($mg.min.\mu mol^{-1}$)**	**CH_4 Selectivity (%)**	**C_2H_5OH Selectivity (%)**	**CO_2 Selectivity (%)**
7500	**1.95**	39.0	13.5	20.9
9600	**1.53**	38.1	7.4	17.1
15000	**0.98**	40.4	8.3	17.0

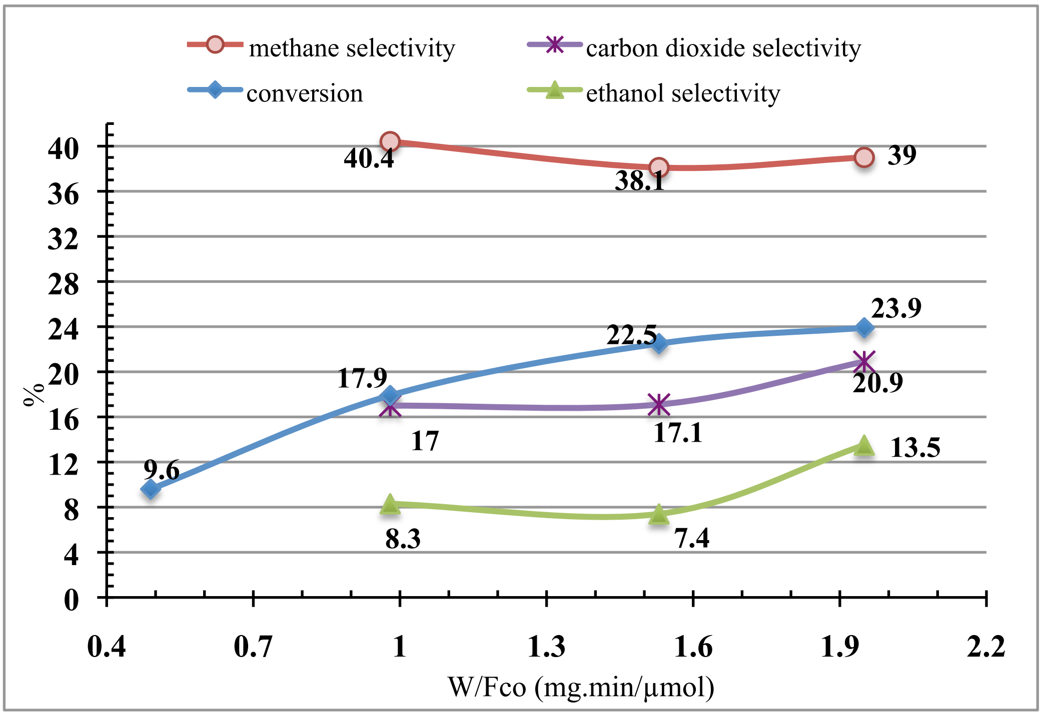


Figure 4.30. Effect of W/F_{CO} ratio on conversion and CH_4, C_2H_5OH, CO_2 selectivity over Rh-La-V/SiO_2 (285°C, 25 bar).

Experiments conducted over 200 mg catalyst with 50 cm^3 total inlet flow rate (i.e the shortest contact time of 0.49 $mg.min.\mu mol^{-1}$) yielded the lowest CO conversion at steady state compared to all other W/F_{CO} ratios tested at 285°C and 25 bar. At a residence time of 0.98 $mg.min.\mu mol^{-1}$, Rh-La-V/SiO_2 gave a CO conversion of approximately 18%. When the W/F_{CO} ratio was increased to 1.53 mg.min.µmol^{-1}, CO conversion was improved and reached approximately 23%. Further increase in residence time up to 1.95 mg.min.µmol^{-1} had a little impact on CO conversion (Figure 4.30).

Regarding product distribution, methane, carbon dioxide and ethanol formations are presented in Tables 4.15 and Figure 4.31. When the residence time was increased from 0.98 mg.min.µmol^{-1} to 1.53 mg.min.µmol^{-1} ethanol production increased slightly from 0.077 µmol/gcat/s to 0.087 µmol/gcat/s. However, at a residence time to 1.95 mg.min.µmol^{-1}, production of ethanol improved remarkably and reached to 0.17 µmol/gcat/s as indicated in Table 4.15. There is no dramatic change in methane and carbon dioxide production with contact time. Formation of both CO_2 and CH_4 increased gradually when residence time was increased from 0.98 mg.min.µmol^{-1} to 1.95 mg.min.µmol^{-1} (Figure 4.31).

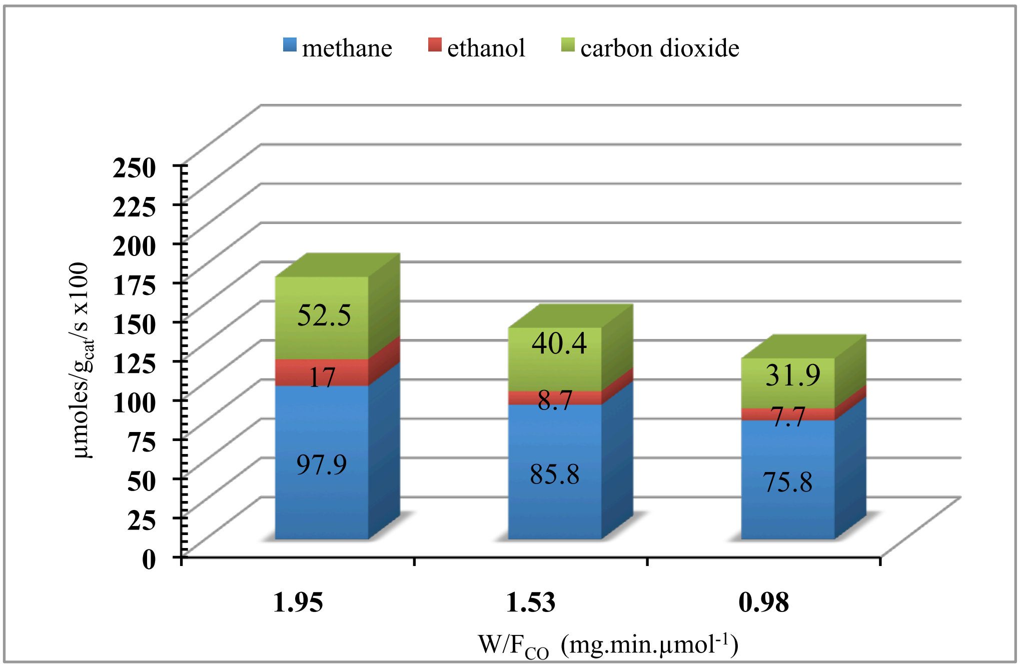


Figure 4.31. Comparison of CH_4, C_2H_5OH and CO_2 production over Rh-La-V/SiO_2 at different W/F_{CO} ratios (285^{0}C, 25 bar).

The highest ethanol selectivity obtained was ca. 14% with 39% methane selectivity at a residence time of 1.95 mg.min.µmol^{-1} (Table 4.16 and Figure 4.31). The selectivity to ethanol was around 7.4% and 8.3% at 1.53 and 0.98 mg.min.µmol^{-1} residence time, respectively. When W/F$_{CO}$ ratio was increased from 0.98 mg.min.µmol^{-1} to 1.53 mg.min.µmol^{-1} methane selectivity decreased from 40% to 38% while the same CO_2 selectivity of 17% was obtained. Increasing the residence time to 1.95 mg.min.µmol^{-1} altered CO_2 selectivity only slightly. The GC-MS chromatograms given in Appendix B (Figure B.4) show product distrubition at 1.53 and 1.95 mg.min.µmol^{-1} residence time.

Subramanian and coworkers (2010) reported that as the space velocity decreased from 36000 to 9000 cm^3/g$_{cat}$ h, CO conversion increased from 0.3% to 8% and selectivity to ethanol and C_{2+} oxygenates also increased at the expense of methanol and methane over Rh-La-V/SiO_2 (14 bar, 270^{0}C). It was claimed that the product distribution shifted toward oxygenates, mainly ethanol, reducing CH_4 formation at space velocity of 9000 cm^3/g$_{cat}$ h. Mei *et al.* (2010) claimed that CO conversion generally decreases with space velocity, by investigating Mn-Rh/SiO_2 catalysts in the 255-305^{0}C temperature range as space velocity varies from 7500 to 15000 cm^3/cm$^3_{cat}$ h. In accordance with results in literature, lower space velocity (W/F$_{CO}$ =1.95 mg.min.µmol^{-1}) used in this work had better impact on CO conversion and ethanol selectivity.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The aim of this study was to develop, prepare and test the CO hydrogenation performance of promoted and silica-supported rhodium catalysts primarily for oxygenated hydrocarbon production using a high-pressure reaction system. Using sequential and/or co-impregnation to incipient wetness of the SiO_2 support, two different catalysts were prepared, namely 1.5wt%Rh-2.6wt%La/SiO_2 and 1.5wt%Rh-2.6wt%La/1.5wt%V/SiO_2. The experimental work involved a parametric study of CO hydrogenation reaction as a function of temperature, pressure and contact time (W/F_{CO}) on V and/or La promoted Rh catalysts.

The major conclusions obtained in this study can be summarized as follows:

- Scanning electron microscopy results indicate that more homogeneous and well-dispersed patterns exist on the surface of doubly promoted (La and V) Rh catalyst in comparison to singly promoted (La) Rh catalyst.

- Singly promoted 1.5wt%Rh-2.6wt%La/SiO_2 catalyst shows poor CO hydrogenation activity, the highest CO conversion achieved (11% at 35 bar and 300^{o}C) being almost one-third of the CO conversion (31%) reached over 1.5wt%Rh-2.6wt%La1.5%V/SiO_2 under the same reaction conditions.

- No significant amount of oxygenated hydrocarbon is produced over Rh-La/SiO_2 whereas ethanol, acetic acid and ethyl ether are the major oxygenated hydrocarbon products obtained over doubly promoted catalyst.

- Reaction temperature has a more pronounced effect on catalytic activity than pressure for both Rh-based silica supported catalysts, conversion and methane selectivity increases as the reaction temperature is increased from 240 to 300^{o}C.

- Experimental data obtained over Rh-La-V/SiO_2 and qualitative observations of the GC-MS chromatograms indicate a more rapid increase in the rate of methane formation relative to oxygenates as reaction temperature is increased.

- Over Rh-La-V/SiO_2 catalyst, higher pressures enhance both formation and selectivity of oxygenated products. Regarding ethanol selectivity, the highest value obtained is ca. 19% at a CO conversion of 9% (270^oC, 35 bar). This is followed by an ethanol selectivity of 15% at 31% CO conversion (300^oC, 35 bar).

- Formation of ethanol is favored in the 270-285^oC temperature range at 25 bar, higher temperatures lead to a decrease in ethanol selectivity. On the other hand, at a higher pressure of 35 bar, the catalyst shows comparable ethanol production performance at 270^oC to that at 285^oC and 25 bar.

- Over Rh-La-V/SiO_2 catalyst, both CO conversion and ethanol selectivity increase when residence time is doubled (24% and 14%, respectively, accompanied by 39% methane selectivity) as indicated by the results obtained at 285^oC, 25 bar and W/F_{CO} ratios between 0.98-1.95 mg.min.μmol^{-1}.

5.2. Recommendations

In the light of the results obtained in the present work, the following studies are recommended as possible future work:

- As the results of this study indicate, elevating reaction pressure within limits has a positive effect on the production of oxygenated products. Higher pressures up to 50-60 bar may be tested to improve activity and oxygenated hydrocarbon selectivity.

- The percent weight of Rh, La and V may be changed to search for better catalytic activity.

- Different supports such as carbon nano-tubes claimed to have exceptional catalytic performance may be used.

- A third promoter can be added to doubly promoted Rh-La-V/SiO_2; most widely reported promoters are manganese and lithium which enhance selectivity to C_2 oxygenates, and/or iridium which suppresses methane formation.

- The gas liquid separator unit of the BTRS may be modified to allow heating up to a temperature where condensation of any vapor product is avoided, for more detailed and reliable product analysis.

APPENDIX A: TOTAL IONIZATION CROSS SESTION METHOD

The ionization cross section method (Fitch and Sauter, 1983) was used for quantification of C_2H_5OH. The equation that relates response factors of target (ethanol) and reference (methane) compounds as follows (Yıldırım, 1993):

$$N_{EtOH} = N_{CH4} \frac{MW_{CH4}}{MW_{EtOH}} \frac{A_{EtOH}}{A_{CH4}} \frac{Q_{CH4}}{Q_{EtOH}} \tag{A.1}$$

where subscript "EtOH" and "CH4" correspond to ethanol and reference compound (methane), respectively. N is the number of moles of species, MW is molecular weight and A is the area obtained from the chromatogram. Q is total ionization cross section. The response factor could be defined as arbitrary peak area per mole of compound.

Since the electron impact voltage of GC-MS is 70 eV, experimental values of total ionization cross sections for ethanol and methane corresponding this voltage were found in literature as follows:

$*Q_{CH4}$= 4.67 (Beran and Kevan, 1969)

$*Q_{EtOH}$= 7.30 (Hudson *et al.*, 2003)

The ratio of peak area of methane to ethanol can be calculated using the GC-MS chromatogram. Since number of moles of methane is determined via calibration curve, ethanol can be quantified using the following equation.

$$N_{EtOH} = N_{CH4} \frac{16}{46} \frac{A_{EtOH}}{A_{CH4}} \frac{4.67}{7.3} \tag{A.2}$$

APPENDIX B: GC-MS CHROMOTAGROMS

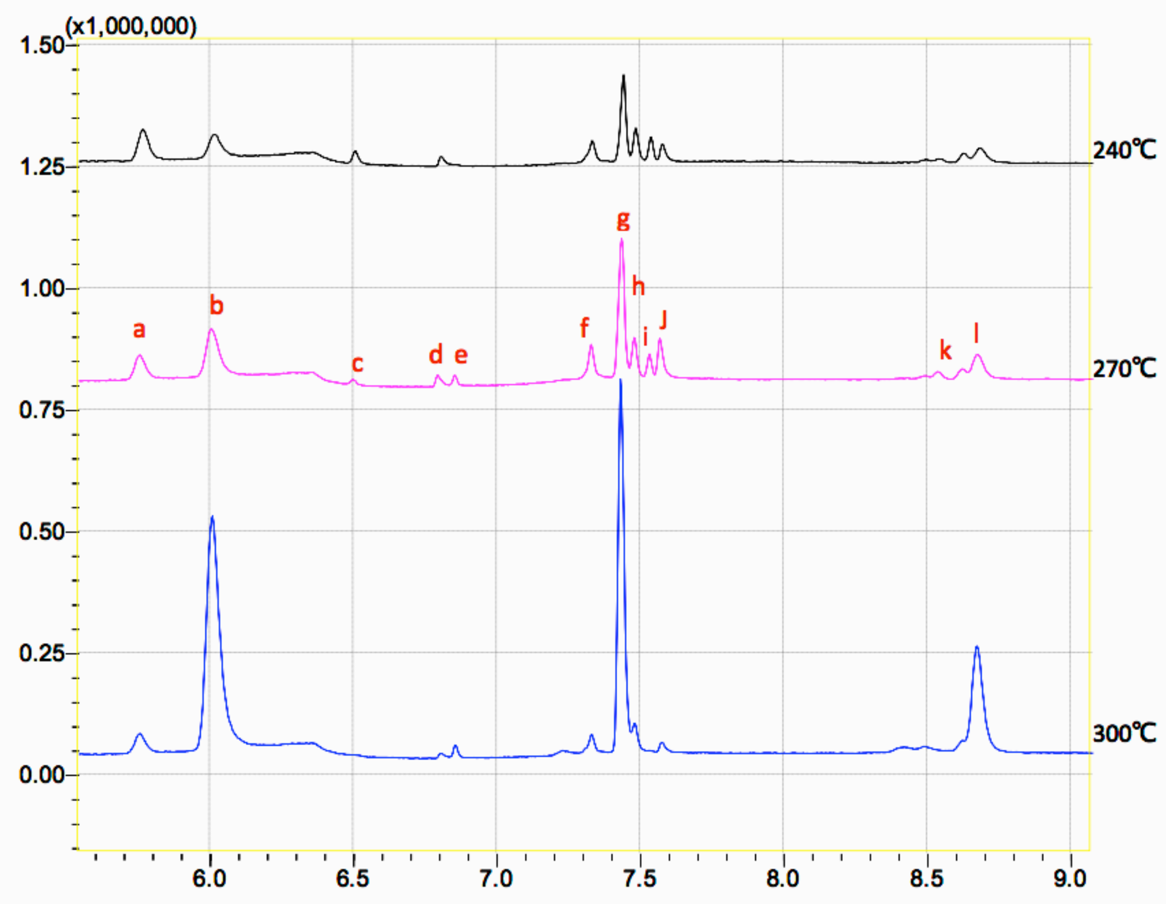


Figure B.1. GC-MS chromatograms for experiments of 240, 270, 300^{0}C at 14 bar

(1.5wt%Rh-2.6wt%La-1.5wt%V/SiO$_2$)

a) Propene, b) Propane, c) Dimethyl ether, d) Methanol, e) Acetaldehyde, f)1-Butene

g) Butane, h) 2-Butene, i) Acetic acid, j) Ethanol, k) Ethyl ether, l) Pentane

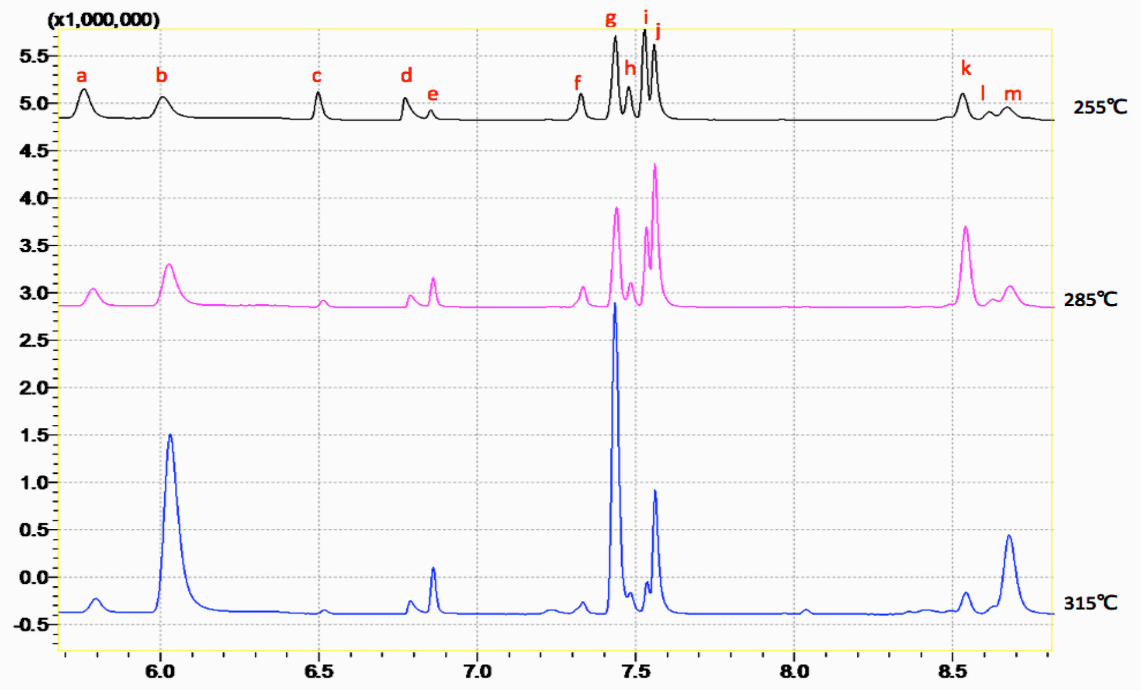


Figure. B.2. GC-MS chromatograms for experiments of 255, 285, 315^0C at 25 bar

(1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2)

a) Propene, b) Propane, c) Dimethyl ether, d) Methanol, e) Acetaldehyde, f)1-Butene, g) Butane, h) 2-Butene,i) Acetic acid, j) Ethanol, k) Ethyl ether, l) 2-Pentene , m) Pentane

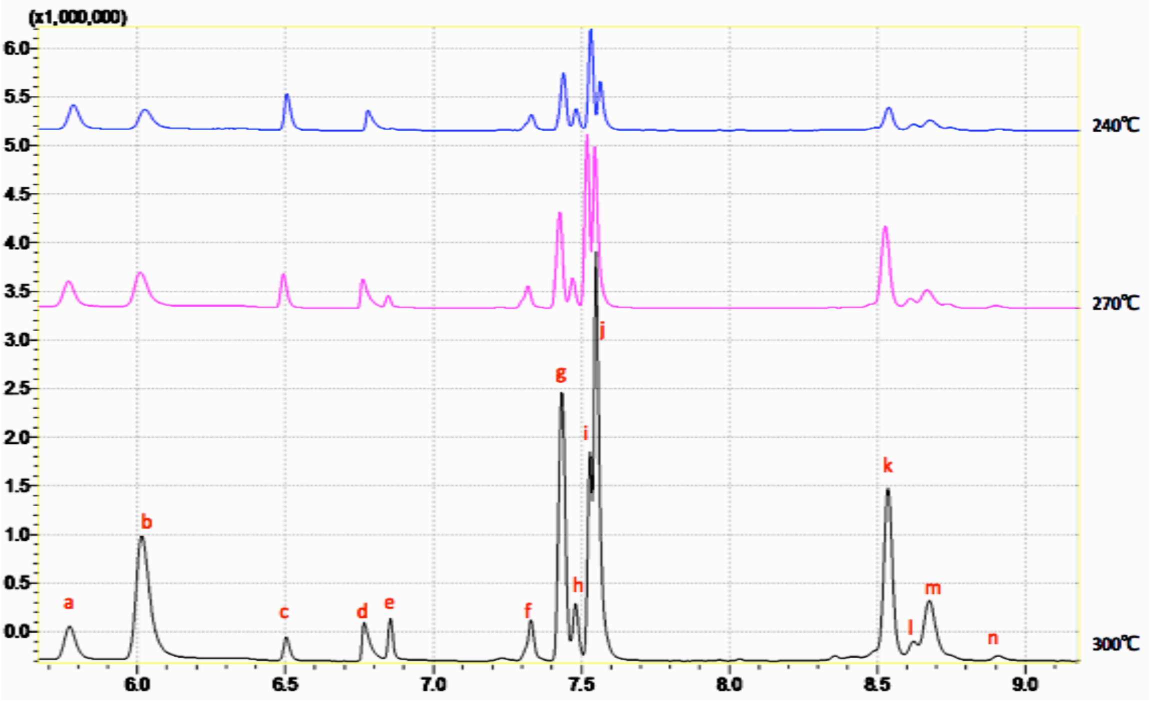


Figure B.3. GC-MS chromatograms for experiments of 240, 270, 300^{0}C at 35 bar (1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2)

a) Propene, b) Propane, c) Dimethyl ether, d) Methanol, e) Acetaldehyde, f)1-Butene g) Butane, h)2-Butene, i) Acetic acid, j) Ethanol, k) Ethyl ether, l) 2-Pentene, m) Pentane, n) Propane, 1-methoxy

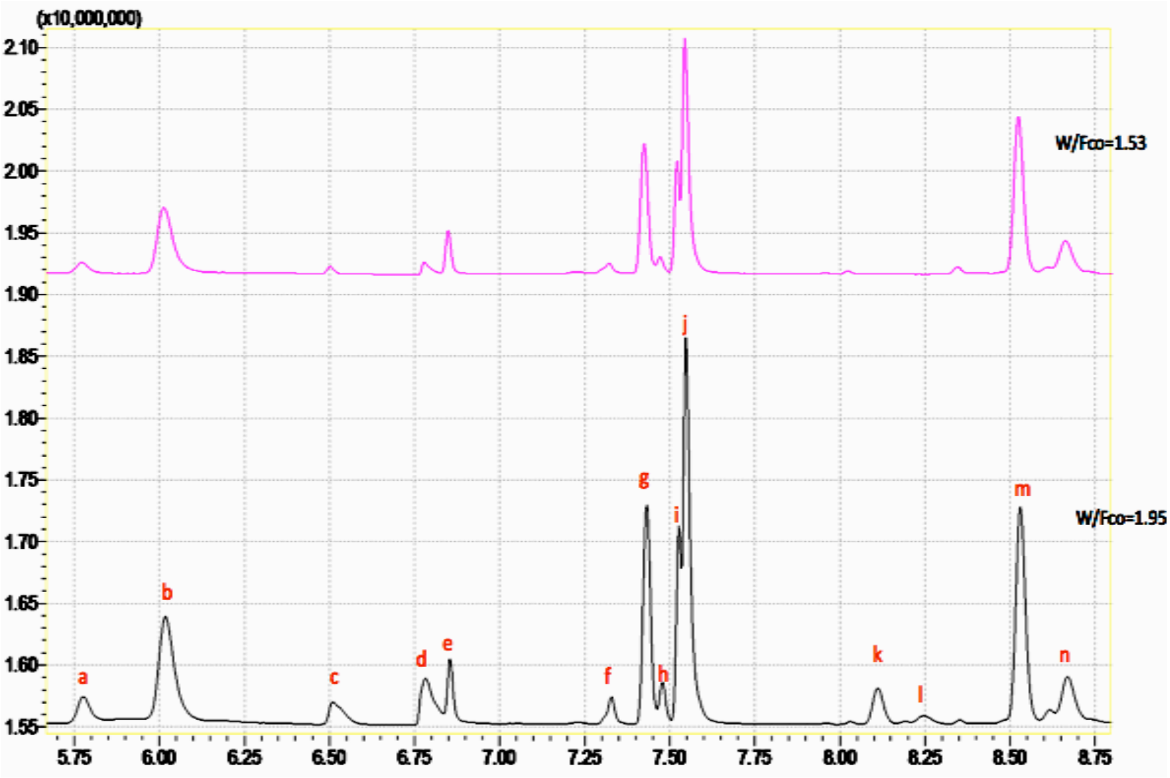


Figure B.4. GC-MS chromatograms for W/F_{CO} of 1.53 and 1.95 mg.min.μmol^{-1}. at 285^{0}C at 25 bar (1.5wt%Rh-2.6wt%La-1.5wt%V/SiO_2)

a) Propene, b) Propane, c) Dimethyl ether, d) Methanol, e) Acetaldehyde, f)1-Butene

g) Butane, h) 2-Butene, i) Acetic acid, j) Ethanol, k) and m) Ethyl ether, l)&n) n-Pentane

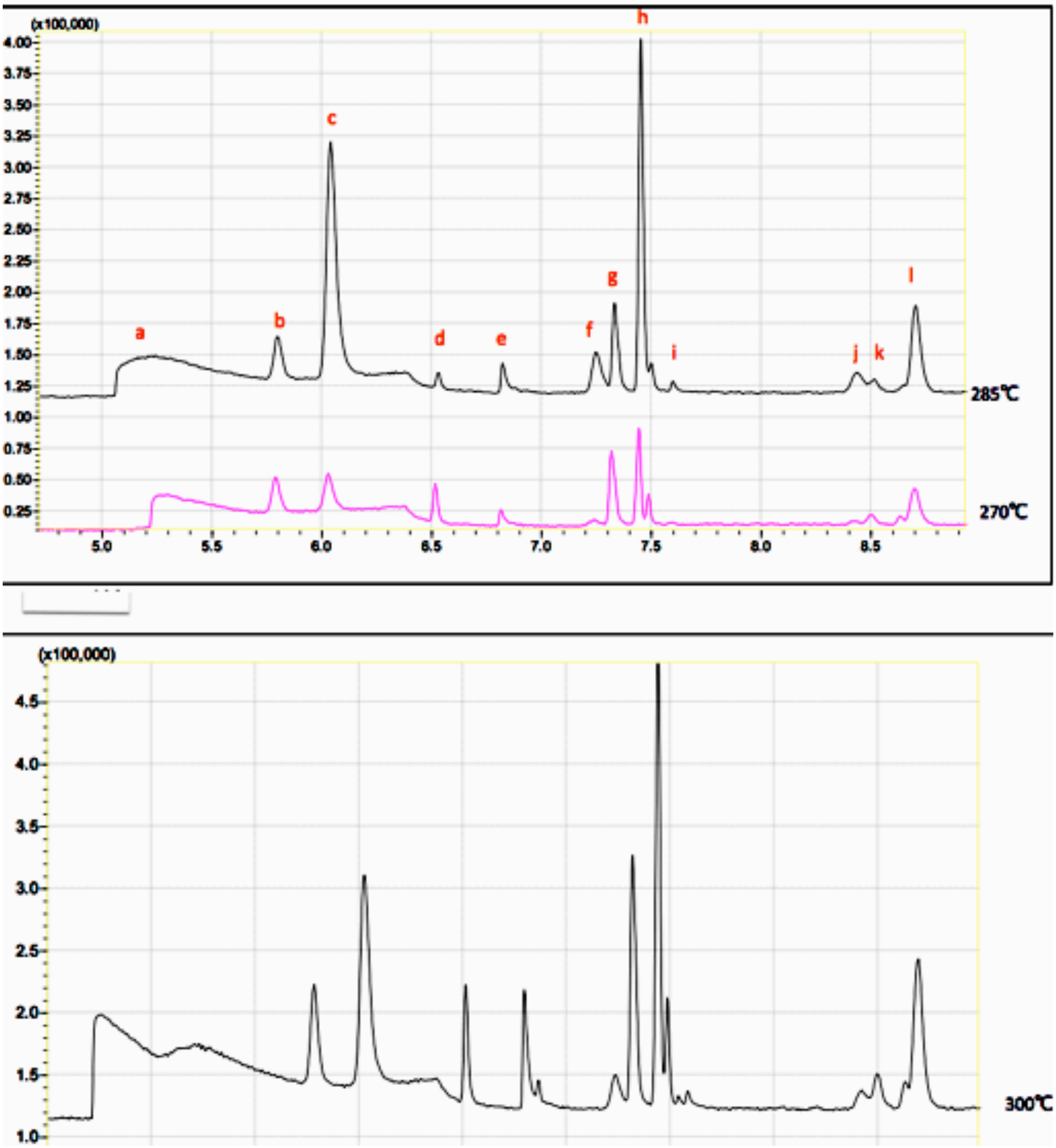


Figure B.5. GC-MS chromatograms for experiments of 270, 285, 300^{0}C at 25 bar

(1.5wt%Rh-2.6wt%La/SiO$_2$)

a) Water, b) Propene, c) Propane, d) Dimethyl ether, e) Methanol, f) Isobutane, f) Butane

g) 2-Butene, h) 2-Butene, i) Ethanol, j) Isopentane, k) 2-Pentene, l) Pentane

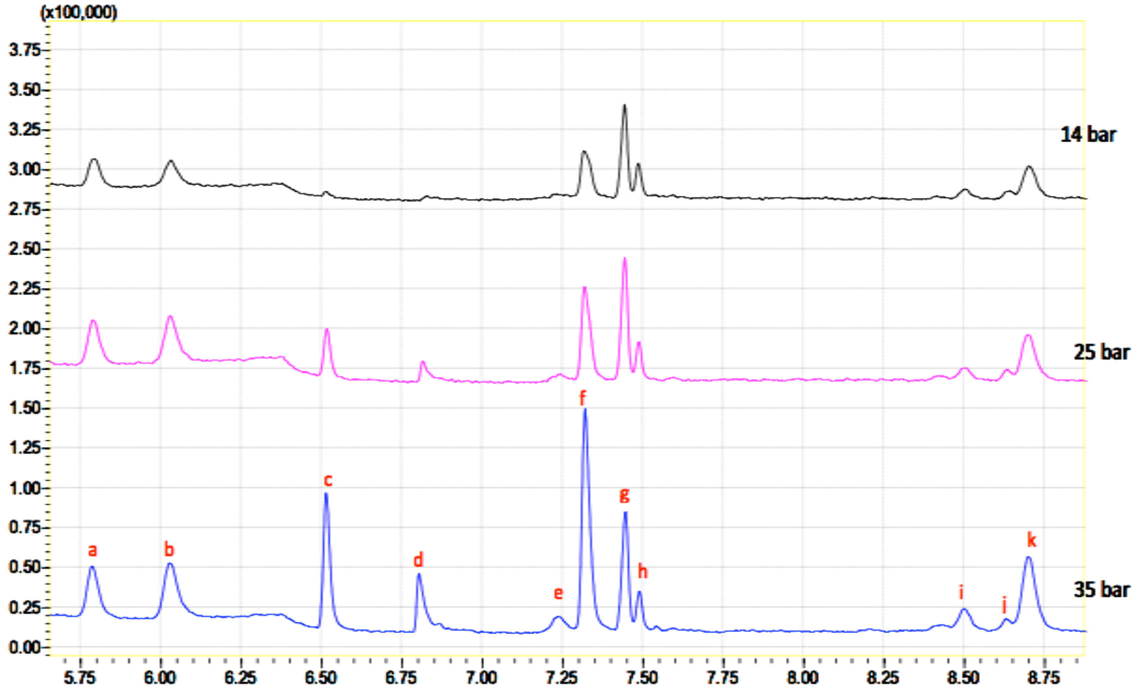


Figure B.6. GC-MS chromatograms for experiments of 14, 25 and 35 bar at 270^0C ($1.5wt\%Rh-2.6wt\%La/SiO_2$)

a) Propene, b) Propane, c) Dimethyl ether, d) Methanol, e) Isobutane, f) Butane, g) 2-Butene, h) 2-Butene, i) Isopentane, j) 2-Pentene, k) Pentane

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