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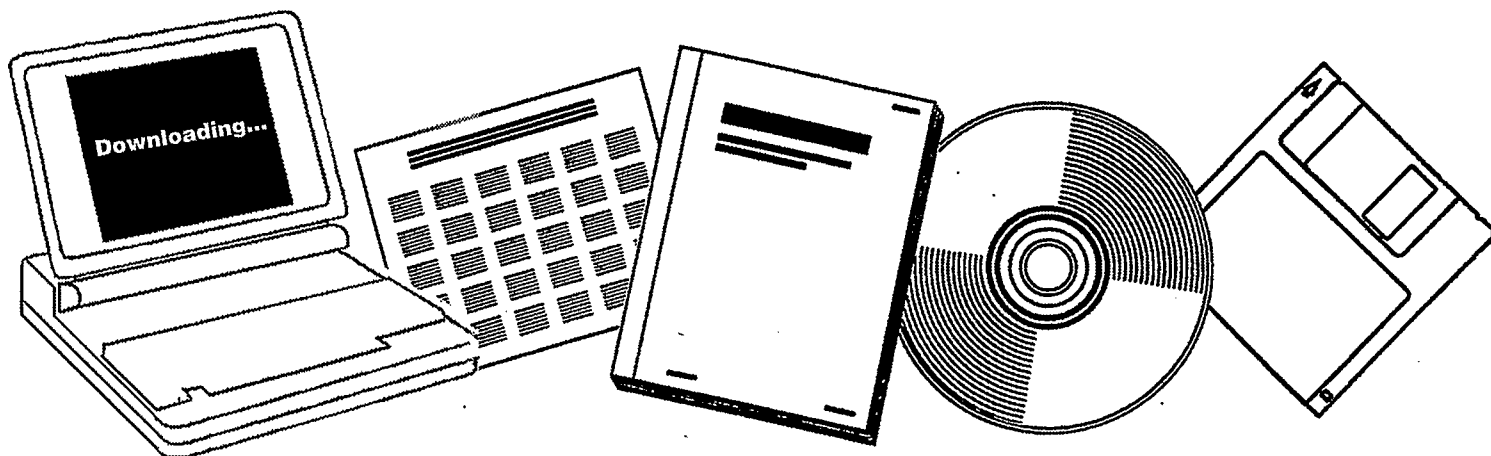
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PROMOTION EFFECTS ON THE SYNTHESIS OF HIGHER ALCOHOLS. FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING

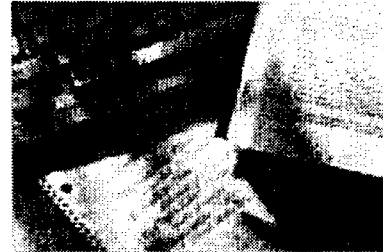
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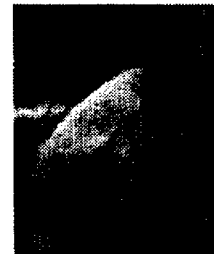
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Final Report

PROMOTION EFFECTS

ON THE

SYNTHESIS OF HIGHER ALCOHOLS

DOE Grant No. DE-FG22-82PC50810

by

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August 30, 1985

OBJECTIVES AND SUMMARY OF RESULTS

The importance of the direct synthesis of higher (C_2-C_6) alcohols from synthesis gas as a promising route for providing clean fuels and petrochemical feedstocks is generally recognized. It is known that the addition of alkali salts to methanol synthesis catalysts increases the production of higher alcohols. However, few investigations have been made into the effect of various alkali species on the synthesis of oxygenates from CO and hydrogen.

A series of research studies have been carried out which greatly expand current knowledge in this area. The objectives of these studies were to investigate the reaction pathways for and the effect of alkali promotion (Li^+ , K^+ , Rb^+ , Cs^+) on the formation of oxygenated compounds from synthesis gas. A series of Group VIII metals (Ni, Ru, Rh, and Pd) and alkali-promoted Rh and Pd catalysts were studied using CO hydrogenation and a chemical probing method with ethylene, ethanol, and acetaldehyde as probe molecules. The chemical probing method developed for this study was demonstrated to be an effective way to (a) identify the possible reaction network occurring on these catalysts, (b) study the interrelationships between oxygenate and hydrocarbon syntheses, (c) determine the catalytic properties of the catalyst surfaces, and (d) investigate support and alkali promotion effects on the reaction pathways to oxygenates and hydrocarbons.

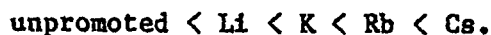
A reaction scheme for the formation of oxygenated compounds and hydrocarbons is proposed. The most probable reaction pathway to C_{2+} oxygenated compounds is insertion of CO into adsorbed C_yH_x species. Both the catalyst ability to catalyze CO insertion and the surface concentration of nondissociatively adsorbed CO are crucial factors for C_{2+} oxygenate formation. Methanol, however, is probably formed directly by hydrogenation of nondissociatively adsorbed CO. It appears that different active sites are

responsible for methanol as opposed to C_{2+} oxygenate and hydrocarbon formation. Due to the fact that C_{2+} oxygenates and hydrocarbons share common intermediates, at least on Ru catalysts, it seems inevitable that hydrocarbons be produced during C_{2+} oxygenate synthesis.

Supports were found to have a great effect on the specific reaction steps occurring during the synthesis over Rh catalysts, i.e., CO insertion, hydrogenation, dehydration, dehydrogenation, and decarbonylation. The CO insertion selectivity was found to decrease in the order: $Rh/SiO_2 > Rh/La_2O_3 > Rh/MgO > Rh/TiO_2 > Rh/Al_2O_3$ while hydrogenation selectivity decreased in the reverse order. The selectivity to C_{2+} oxygenates parallels that for CO insertion but does not correlate with the acidity/basicity of the support.

Suppression of hydrogenation and ethanol dehydration was identified as a major effect of alkali promotion of Rh catalysts. The combined effects of promoters and supports are not simply the superposition of these two effects. Specific steps, i.e., CO insertion, decarbonylation, and hydrocarbon chain growth, were found to be dependent upon both the nature of the alkali promoter and that of the support.

In general, all product formation rates decreased upon promotion. The order of this decrease was



While all these rates decreased upon promotion, the rate of hydrogenation decreased faster than that of CO insertion resulting often in increased selectivities for C_{2+} oxygenates.

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1.0 INTRODUCTION

1.1 General Introduction

The importance of the direct synthesis of oxygenated compounds, especially higher alcohols, from synthesis gas as a promising route for providing clean fuels and petrochemical feedstocks is generally recognized. Approaches to the synthesis of oxygenated compounds have included the use of catalysts based on (a) supported metal catalysts, such as Fe^(1*,2), Co⁽³⁾, Ru⁽⁴⁾, and Rh^(5,6), or (b) Cu/ZnO based catalysts.^(7,8,9) The synthesis of oxygenated compounds over Cu/ZnO based catalysts⁽⁷⁾ requires the use of high pressures (at least 60 atm), while the synthesis of C₂ oxygenates such as ethanol has been found to occur over Rh catalysts at subatmospheric and low temperature conditions (180-220°C).⁽¹⁰⁾ Synthesis at low temperatures and pressures appears to be much more attractive than that at high pressures and moderate temperatures. However, because of high price of Rh metal, Rh related catalysts must show high selectivity and activity for the formation of oxygenated compounds and resistance to deactivation in order to be economically feasible for the commercial production of oxygenated compounds. This requires an improvement in our current knowledge of the mechanism of oxygenate synthesis, promotion effects, and support effects; none of these are well understood. In addition to the practical importance of Rh catalysts for oxygenate synthesis, the unique property of Rh for the production of both hydrocarbons and oxygenates^(5,6) suggests its use as a model

*Parenthetical references placed superior to the line of text refer to the bibliography.

catalyst to study mechanisms of oxygenate and hydrocarbon formation and to investigate support and promotion effects on the selectivity of CO hydrogenation.

1.2 Thermodynamics of Oxygenate Synthesis

The change in Gibbs free energy at 600°K during the formation of linear alcohols and hydrocarbons from synthesis gas is shown in Figure 1-1. Since change in Gibbs free energy for the formation of hydrocarbons is more negative than that for the formation of alcohols, alcohol synthesis requires the use of a selective catalyst to preclude the reaction from proceeding further downhill on the thermodynamic scale. High pressure is also needed to achieve a desirable degree of conversion of synthesis gas to oxygenated compounds. Figure 1-2 shows the dependence on temperature of Gibbs free energy change for the formation of certain oxygenates and hydrocarbons from synthesis gas. The Gibbs free energy change associated with the formation of oxygenated compounds increases rapidly with temperature so that conditions which favor oxygenate formation are at low temperatures.

1.3 Reaction Mechanisms

The proposed reaction mechanisms for the formation of oxygenated compounds from synthesis gas can be summarized in Figure 1-3. Although there still exists a controversy about the nature of the intermediates to oxygenated compounds, it is generally agreed that

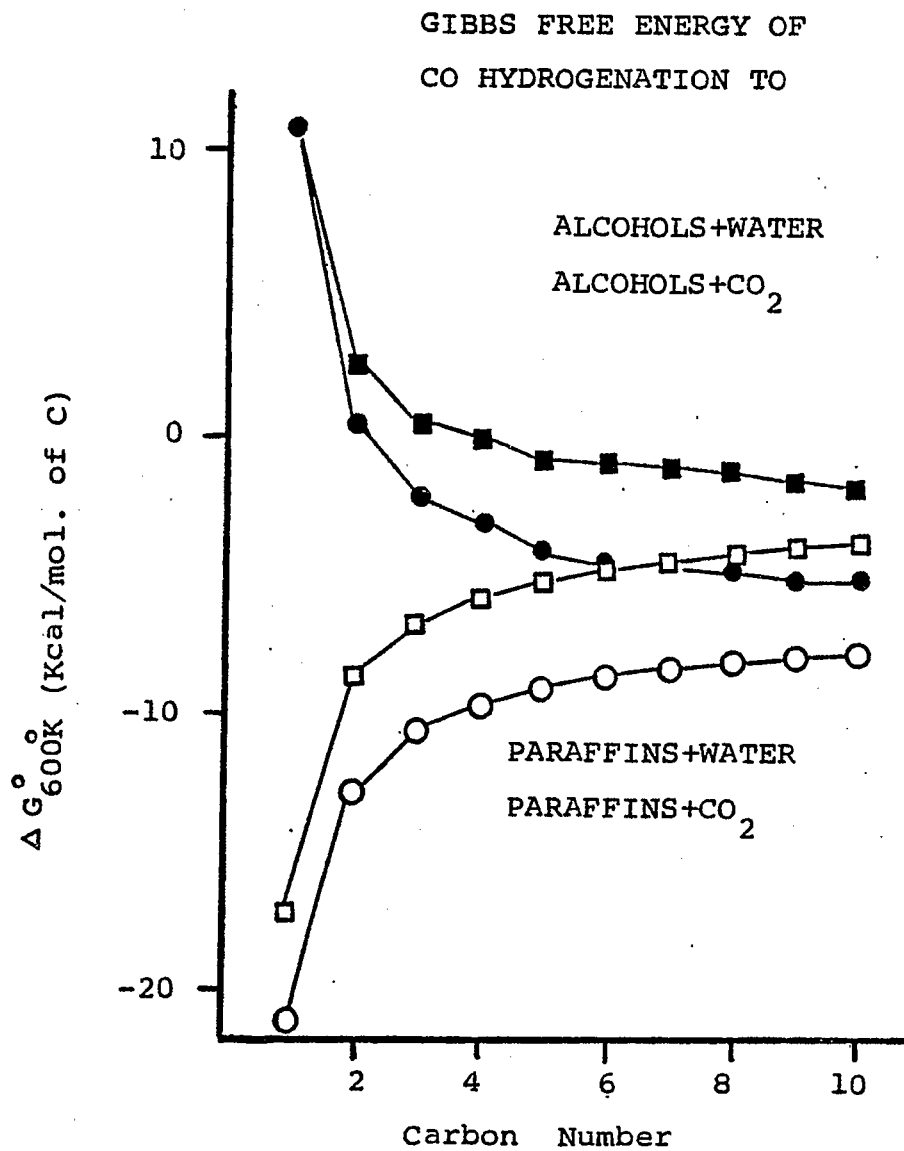


Figure 1-1 Change in Gibbs Free Energy at 600 K for the Formation of Linear Alcohols and Hydrocarbons from CO/H₂

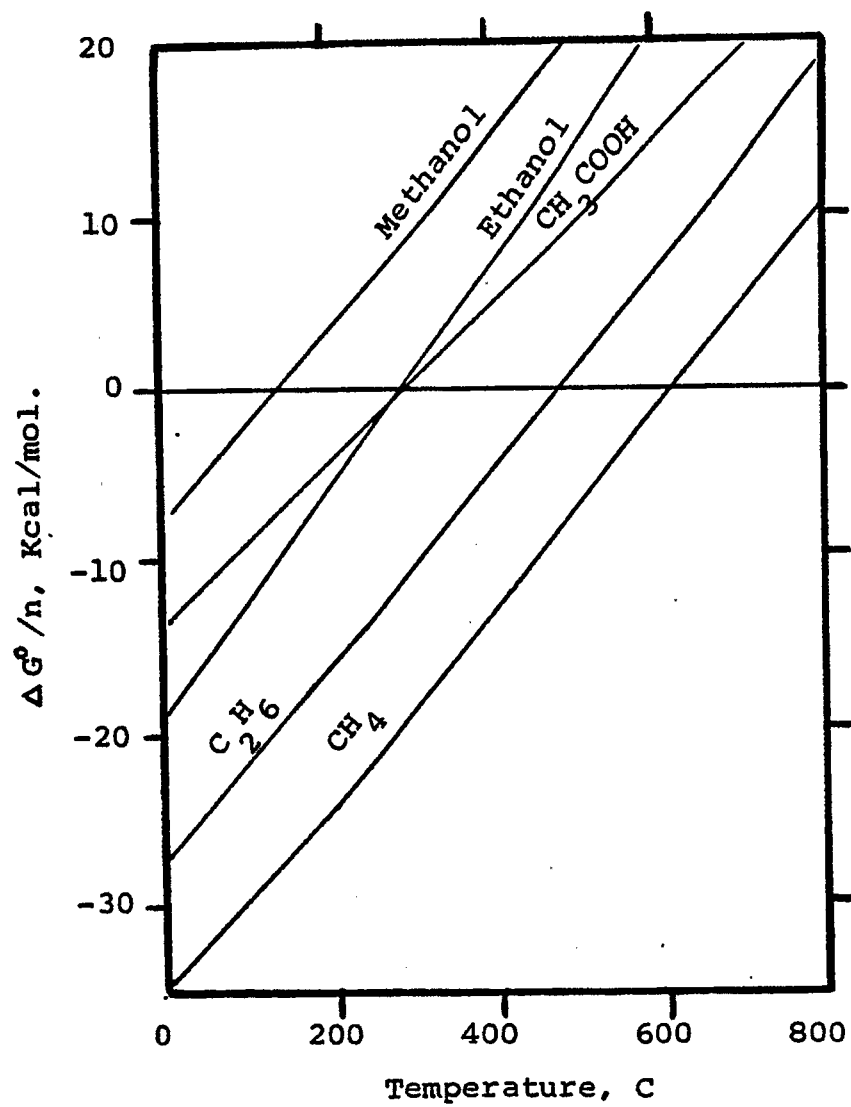


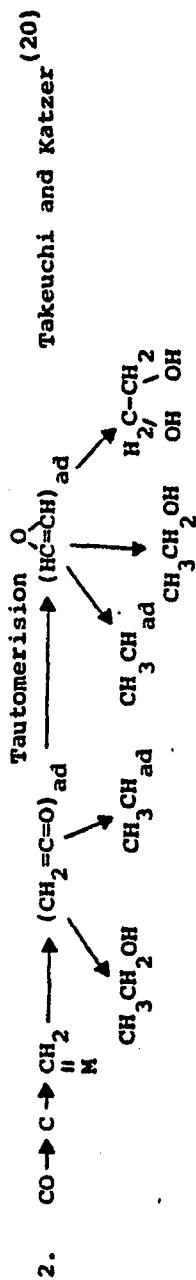
Figure 1-2 Gibbs Free Energy Change for the Formation of Oxygenates and Hydrocarbons from CO/H_2 as a Function of Temperature

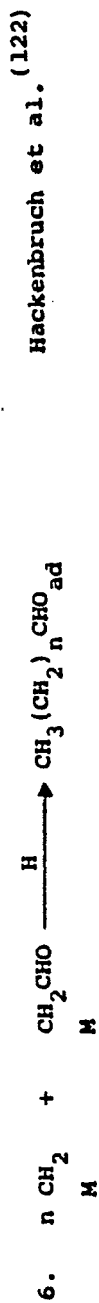
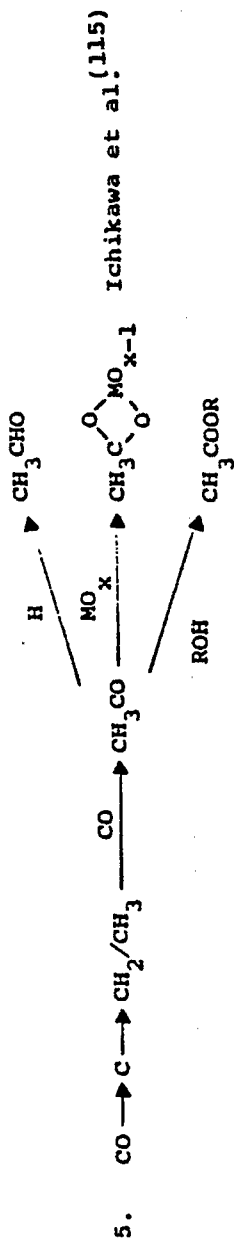
Figure 1-3 Proposed Mechanisms for the Formation of Oxygenates from CO/H₂

A. Proposed Mechanism for C₂ Oxygenate Synthesis

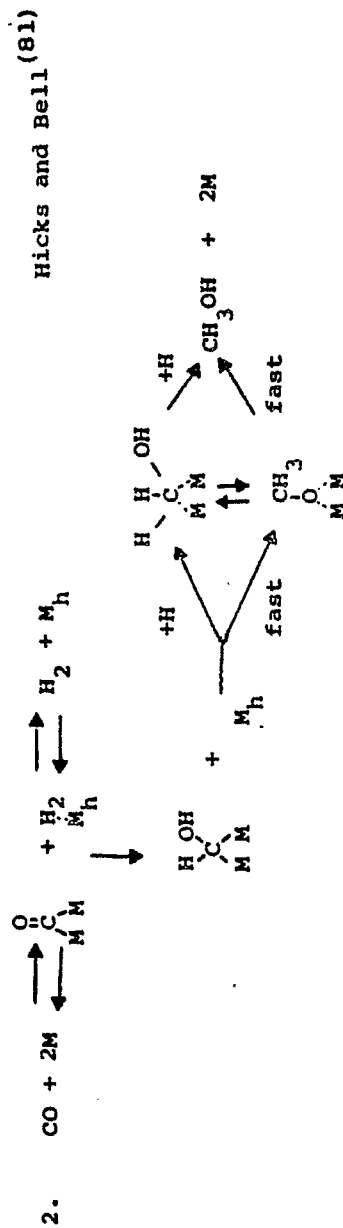
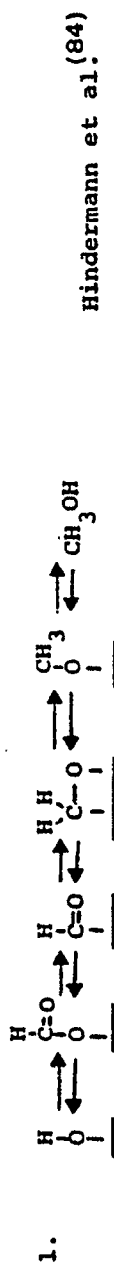


CO insertion on Rhodium Oxide

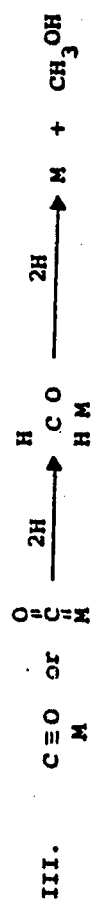
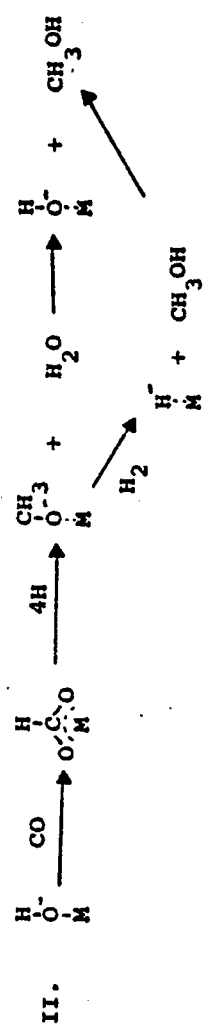
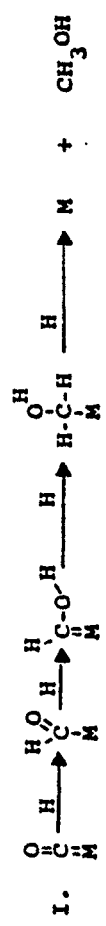




B. Proposed Mechanisms for Methanol Synthesis



3. The proposed mechanisms may be divided into three groups. Klier (7)



formation of methanol involves hydrogenation of nondissociatively adsorbed CO and formation of C_{2+} oxygenated compounds involves the insertion of CO into adsorbed C_yH_x species which are generated by CO dissociation followed by hydrogenation. It has also been proposed that CO insertion into surface alkyl groups is a chain termination step during the Fischer-Tropsch synthesis.^(17,24) On the other hand, this step has also been proposed as a chain propagation step in the FT synthesis.⁽²⁶⁻²⁸⁾ Recently, van den Berg⁽²⁹⁾ showed that the reduction of acyl or hydroxyalkyl groups to alkyl groups is slow on Mn-Mo-Rh/SiO₂. This may suggest that CO insertion to form oxygen-containing intermediates may not be a major route for chain propagation over Rh catalysts. However, this CO insertion step still can not be completely ruled out as a chain propagation step. Rofer-DePoorter⁽³⁰⁾ has pointed out that the network character of the FT mechanism makes it difficult to separate one path from the other, since many paths have common intermediates; one path does not necessarily preclude the other.

1.4 Catalysts

Based on our current knowledge of mechanisms of oxygenate formation, the general requirements for a catalyst to catalyze oxygenate formation from CO and H₂ can be summarized as following.

Methanol Synthesis

- inability to dissociate CO.

- high hydrogenation ability coupled with an ability to activate nondissociatively adsorbed CO.⁽⁷⁾

C₂+ Oxygenate Synthesis

- moderate CO dissociation ability permitting the existence of both surface carbon and nondissociatively adsorbed CO on the catalyst surface.⁽⁶⁾
- ability to catalyze CO insertion into adsorbed C_yH_x species.⁽¹¹⁾

For group VIII metals, there exists a relationship between their position in the periodic table and their ability to chemisorb CO dissociatively. This relationship has been established by Broden et al.⁽²¹⁾ as shown in Table 1-1. Metals on the right hand side of the 200-300°C line, such as Pd, Pt, Ir, are not active for CO dissociation. These metals have also found to be good methanol synthesis catalysts. Metals on the left hand side of the ambient temperature line are active for CO dissociation at room temperature. These metals, such as Fe, are active for hydrocarbon synthesis. Metals between these two lines have moderate CO dissociation ability and only dissociate CO at synthesis temperatures (200°C-300°C). These metals on the border of the center and group on the right appear to be good candidates for C₂ oxygenate synthesis.⁽⁶⁾ In addition to the dependence of CO dissociation ability on the position of metal in the periodic table, both CO dissociation ability and catalytic ability of metal also depend on the chemical and physical state of the metal. Factors which affect the state of metal catalysts include dispersion,

Table 1-1 CO Chemisorption on Transition Metals

VI	VII	VIII			IB
CR	MN	FE	CO	NI	CU
MO	Tc	RU	RH	PD	AG
W	RE	OS	IR	PT	AU

AMBIENT TEMPERATURE SYNTHESIS TEMPERATURES
 200-300°C

the type of support, promoter, and impurities. Details about the effects of alkali promoters and supports will be discussed later.

1.5 Active Sites for Oxygenate Formation

Due to the difficulty in characterizing the state of the catalyst surface under reaction conditions, it is still not clear what type of active sites is responsible for oxygenate formation. Watson and Somorjai⁽³²⁾ have suggested that CO insertion to form C₂ oxygenates occurs on Rh⁺ sites while CO dissociation and hydrogenation takes place on Rh metal sites. Orita et al.⁽²⁵⁾ proposed that the active sites for the formation of C₂ oxygenates may be located at the interface of Rh and the support. It has also been hypothesized⁽²⁹⁾ that Rh ions may be stabilized at the metal-oxide support interface. Rh⁺ has been observed on Rh/SiO₂ which is able to catalyze the formation of C₂ oxygenates⁽²⁹⁾ and on Rh/MgO⁽³³⁾ which is active in the formation of methanol⁽⁶⁾. Iwasawa et al.⁽³⁴⁾ reported that Rh/SiO₂, which had been pretreated with H₂/H₂O, produced a higher yield of oxygenates than that pretreated with H₂ alone. It was speculated that the different pretreatment on Rh catalysts may lead to different oxidation states of Rh. On the contrary, Katzer et al.⁽⁶⁾ reported from a XPS study that there was no evidence for the existence of Rh⁺ on Rh/TiO₂ which is known to be active for the formation of C₂ oxygenates. Ponc⁽⁸⁰⁾ also found no correlations of the selectivity to oxygenates to the amount of Rh⁺ present, contrary to what was found for Pd catalysts. Conflicting suggestions on the type of Pd sites

responsible for methanol formation also exist. Poels⁽⁶²⁾ suggested that Pd^+ is the active site for methanol synthesis while Hicks and Bell⁽⁸¹⁾ proposed that Pd metal is important for methanol formation.

While questions concerning the active sites for the formation of oxygenated compounds remain, the formation of hydrocarbons is generally considered to be by CO dissociation followed by hydrogenation on Rh metal sites. CO dissociation has been shown to require a large ensemble of surface atoms^(17,35), and it is a structure sensitive reaction step.⁽³⁶⁾ However, hydrogenation of surface carbon species does not seem to require such an ensemble. Hydrogenation of olefins is also well known to be structure insensitive⁽³⁷⁾. Recently, Boudart and McDonald⁽³⁶⁾ have suggested that CH_x insertion into surface alkyl groups should require a larger ensemble as the active site than that required for CO dissociation. Much has been done on the structure sensitivity of hydrocarbon synthesis; however, the requirements for active sites for the formation of oxygenated compounds over heterogeneous metal catalysts have never been studied. Based on an analogy with organometallic chemistry⁽³⁸⁾, it is possible that CO insertion into a surface methyl group may occur on a single atom site.

1.6 Effects of Alkali Promotion

While the literature on the effect of alkali promotion on CO hydrogenation is voluminous^(2,16,39-43), little has been done in developing an understanding of the effect of alkali promotion on

oxygenate synthesis from CO and H₂, especially over Rh catalysts. Alkali promoters are known to modify the activity, selectivity, and stability of catalysts⁽¹⁶⁾. The effect of alkali promotion on CO hydrogenation over a number of group VIII transition metal catalysts, such as Ni^(44,45), Ru^(46,47), Pd⁽⁴⁸⁾, Rh^(13,14) and Fe⁽²⁾ can be summarized as resulting in (a) an increase in the CO dissociation probability over Ni^(49,50,51), Ru⁽⁵²⁾, Fe^(53,54,55), Rh⁽⁵⁶⁾, (b) a suppression of hydrogenation ability for all the cases, (c) an increase in selectivity to olefinic and long chain hydrocarbons, (d) an increase in oxygenate selectivity for Rh^(13,14), Pd⁽⁴⁸⁾, and Fe⁽²⁾, and (e) modification of catalytic activity. The initial chemical state of alkali promoter during the preparation of alkali-promoted catalysts does not seem to affect the extent of alkali promotion.⁽⁵⁷⁾ Addition of alkali species in various forms, such as the oxide, carbonate, or nitrate, to supported iron catalysts has been demonstrated to produce similar results.⁽²⁾ However, the effect of alkali promotion does depend on the type of alkali cations and the loading of the alkali promoter.^(41,58)

A number of investigators have tried to elucidate the mechanism for alkali promotion by studying CO and H₂ chemisorption on alkali-promoted catalysts or alkali doping of metal single crystals. Dry et al.⁽⁴¹⁾ have suggested that alkali species, which are strong bases, tend to donate electrons to neighboring metal atoms. This argument has long been applied to interpret the increase in the CO adsorption energy and dissociation probability on alkali-promoted catalysts.

Several surface science studies^(43,50,51) have shown that the doping of K metal on transition metal surfaces results in a decrease in work function and an increase in the electron emission capability of the metal surface. These are considered as a consequence of the electron transfer from the alkali metal promoter to the transition metal atoms.⁽⁵⁹⁾ These studies also showed that alkali species enhance CO adsorption and dissociation.

Although the surface science studies seem to support the argument for charge transfer from alkali promoters, it is unlikely that alkali species would exist in the metal form under synthesis conditions.⁽⁶⁰⁾ It should be emphasized that alkali ions should not have the ability to donate electrons to metals.⁽⁶²⁾ Praliaud et al.⁽⁴⁴⁾ have observed from an XPS study that potassium remains as K^+ after reduction of KNO_3-Ni/SiO_2 . They suggested that K^+ may be present in the form of a K-O-Ni surface complex resulting in the observed shift in binding energy of Ni $2P_{3/2}$ electrons. They have further suggested that the shift in binding energy of Ni is due to a transfer of electrons from K oxide to Ni metal. It has been suggested that both alkali oxide and alkali metal have electron donating characteristics, although such a characteristic is less significant for alkali oxide than alkali metal.⁽⁷⁶⁾ It was observed that adsorbed KOH on iron causes a similar increase in the CO adsorption energy as elemental K does.⁽⁶¹⁾ Bonzel⁽⁴³⁾ has suggested based on his XPS data that K may exist as KOH after reduction of KNO_3-Fe foil. He also suggested that KOH could be transformed into K_2CO_3 or KCO_2 after CO

hydrogenation. He further suggested that the promotion effect is mainly due to K^+ and not the anion, which may change with the chemical environment. The controversy about the mechanism of alkali promotion still exists. Determination of the chemical state of alkali promoters during synthesis appears to be crucial in elucidating the mechanism for alkali promotion.

Hydrogen chemisorption suppression on alkali-promoted catalysts has been reported for Ru⁽⁶³⁾ and Pt/TiO₂⁽⁶⁴⁾. It was observed in single crystal studies that alkali promoters increase the adsorption energy of H₂ but decrease the sticking coefficient of H₂ on Ni⁽⁵⁰⁾ and on Fe.⁽⁶⁵⁾ On the contrary, Benziger and Madix⁽⁶⁶⁾ reported that K promotion increases both the adsorption energy and the sticking coefficient of H₂ on Fe. Although results from hydrogen chemisorption are not abundant and consistent in the literature, hydrogenation suppression due to alkali promotion leading to low methane, high olefin, and high hydrocarbon selectivities has been well documented.⁽⁴⁴⁻⁴⁷⁾ Campbell and Goodman⁽⁴⁵⁾ have pointed out that the decrease in methanation activity as a result of K promotion must be related to a poisoning of either the hydrogen adsorption or hydrogen addition steps. The increase in CO adsorption energy brought about by alkali promotion may also contribute to the hydrogenation suppression since high coverages of CO or a surface carbide is known to decrease the rate of hydrogen adsorption.⁽⁶⁷⁾

Campbell and Goodman⁽⁴⁵⁾ have also suggested that the decrease in hydrogenation ability caused by alkali promotion would lead to more

carbon present on the surface resulting in greater chances for the formation of higher hydrocarbons. Besides the chemical effect of alkali promoters, it is expected that these promoters may block the active sites for reactions. However, the physical blockage effect of alkali promoters would not appear to be a major factor for alkali promotion since alkali promoters are able to greatly enhance the structure sensitive CO dissociation step and significantly suppress the structure insensitive hydrogenation step.

While it is well known that the addition of alkali promoters to iron catalysts results in an increase in oxygenate yields (16), the effect of alkali promotion on the formation of C₂ oxygenates over Rh has been only recently studied.^(13,14) Kagami et al.⁽¹³⁾ suggested that the active sites for the formation of C₂ oxygenates are located at the interface of the metal and the support and that modification of this interface by alkali species promotes the formation of C₂ oxygenates. Poels⁽⁶²⁾ proposed that alkali promoters may (a) stabilize some metal ions against reduction and (b) create a defect structure which could be beneficial for the activity of catalysts.

1.7 Effects of Support

The catalytic properties of a metal can be modified by not only the addition of a promoter but also by the use of a support. It has been reported that the selectivity of CO hydrogenation over supported rhodium catalysts varies with the basicity of the support.^(6,12) Rh on MgO, a very basic support, exhibits a 90% selectivity to

methanol. Acidic supports, such as Al_2O_3 , result mainly in CH_4 formation, while slightly acidic or basic supports (e.g., SiO_2 , TiO_2 , CeO_2) produce both alcohols and hydrocarbons. It appears that the observed differences in product selectivity and activity over various supported Rh catalysts are due to modification by the support of the catalytic ability of Rh for CO dissociation, hydrogenation and CO insertion. Recently, Edrohelyi and Solymosi⁽⁶⁸⁾ have reported that the effect of the support in promoting the dissociation of CO over Rh decreases in the order: $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{MgO}$. It may be expected that oxygenated compound selectivity would follow the reverse order. Katzer et al.⁽⁶⁾ have reported, in fact, that alcohol selectivity over Rh catalysts increases in the order: $\text{TiO}_2 < \text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{MgO}$. Edrohelyi and Solymosi⁽⁶⁸⁾ have also reported that the activation energy for the hydrogenation of reactive surface carbon increased in the order: $\text{Rh/TiO}_2 < \text{Rh/Al}_2\text{O}_3 < \text{Rh/SiO}_2$. However, little is known about the effect of the support on the CO insertion step during CO hydrogenation.

In addition to the above direct effects of alkali promoters and supports on a metal, the alkali promoters may modify the properties of a support resulting in an indirect promotion of the metal via the support. It has been reported that part of the added potassium promoter tends to be attached to the high surface area support rather than the small metal particles.⁽⁶⁹⁾ The most obvious effect of alkali promoters on the support properties is to alter the basicity/acidity of the support. Alkali promoters have been used to neutralize the

acid centers and/or create basic centers on catalysts.⁽⁴²⁾ Since the formation of alcohols over Rh catalysts can be promoted by the use of basic supports or of alkali promoters when the Rh is supported on an acidic support, e.g., Al_2O_3 ⁽¹³⁾, it would be useful to be able to determine whether direct alkali promotion or indirect alkali promotion via the support is predominant on alkali-promoted Rh catalysts.

1.8 Objectives and Scope of this Study

A number of mechanisms have been proposed to explain alkali promotion of oxygenate synthesis.^(1,2, 6-20, 40-46) Due to a lack of understanding of basic factors controlling the formation of oxygenated compounds, the effect of alkali promotion on oxygenate synthesis is still far from being understood. This study utilizes the fact that Rh is able to catalyze the formation of both oxygenated compounds and hydrocarbons to investigate the effects of alkali promotion and of the nature of the support on oxygenate synthesis. This work was undertaken in order to help provide answers to the following questions:

Product Distributions

- What are the basic factors controlling product distribution from CO hydrogenation over group VIII metals?
- What are the reaction pathways for the formation of oxygenated compounds and hydrocarbons from synthesis gas?

Support and Alkali Promoter Effects on Rhodium Catalysts

- How do supports and alkali promoters affect reaction pathways of CO hydrogenation over rhodium catalysts?
- How do interactions among metal, support, and alkali promoters affect the properties of rhodium?

Relationship Between Methanol Synthesis and C₂ Oxygenate Synthesis

- Is there any link between the synthesis of methanol on Rh and on Pd?
- How do pretreatment conditions affect oxygenate synthesis over Rh/MgO?

A probe molecule technique has been developed to investigate aspects of the reaction pathways for oxygenate formation and the effects of promoters and supports on the chemical properties of Rh metal. Details of this technique are reported in Chapter 2.

The reaction pathways for the formation of oxygenated compounds and hydrocarbons from CO hydrogenation over group VIII metals were examined using silica-supported Ni, Ru, Rh, and Pd catalysts since these catalysts are able to produce distinct product distributions with respect to one another. This study has provided us with a better understanding of mechanisms of hydrocarbon and oxygenate compound formation. Results of this study are reported in Chapter 3. Chapter 4 reports on results of an investigation of support effects on the properties of Rh catalysts. Catalysts utilized for this study included Rh black and Rh supported on Al₂O₃, TiO₂, SiO₂, La₂O₃, and MgO.

The effect of alkali promotion on C_2 oxygenate synthesis was investigated in a systematic study of various alkali-promoted Rh/TiO₂, Rh/Al₂O₃, Rh/SiO₂, Rh/La₂O₃, Rh/MgO, and unpromoted Rh catalysts. Results of this investigation are presented in Chapter 5-7. Chapter 8 reports on results of a study of the effect of K promotion on methanol synthesis over Pd/SiO₂. Results of methanol synthesis over Rh and Pd catalysts are summarized in Chapter 9. This investigation aim at elucidating factors controlling methanol synthesis and C_2 oxygenate synthesis.

Overall this study has sought to establish a better understanding of support effects and alkali promotion effects on oxygenate synthesis. The results of this study and their significance for catalysis are discussed and summarized in Chapter 10.

2.0 EXPERIMENTAL

2.1 Catalyst Preparation and Characterization

Ru/SiO₂ was prepared by ion exchange using Ru(NH₃)₆Cl₃. Ru(NH₃)₆Cl₃ was dissolved in a weak acidic HCl solution (PH = 4.5). This solution was then mixed with SiO₂ (the solid to liquid ratio = 5 gram/liter) and stirred at room temperature for 50 hours to proceed ion exchange process. After ion exchange process, the catalyst was filtered and washed several times by deionized water and then dried in air for 18 hours.

Ni/SiO₂ was prepared by the incipient wetness method using an aqueous solution of NiCO₃.

Alkali-promoted Rh catalysts were prepared by impregnation of various supports using RhCl₃·3H₂O (Alfa Products) and an alkali nitrate (Li, K, Cs) in aqueous solution at pH = 3-3.5. The supports for these catalysts included Al₂O₃, TiO₂, SiO₂, La₂O₃, and MgO. The atom ratio of the particular alkali element to Rh was 1/2. Unpromoted supported Rh catalysts were also prepared in the same way except that alkali species was not added.

Pd/SiO₂ catalysts were prepared by impregnation using PdCl₂. Potassium-promoted Pd/SiO₂ catalysts were prepared by subsequent impregnation of Pd/SiO₂ using a KNO₃ solution resulting in atom ratios of K to Pd of 0.6 and 1.8.

The source and compositions of oxide supports used for preparation of these catalysts are listed in Table 2-1. After

Table 2-1 Sources and Compositions of Catalyst Supports

Catalysts	Sources	Compositions
TiO ₂	Degussa	Primary anatase
SiO ₂	stream	-
Al ₂ O ₃	stream	γ-Al ₂ O ₃
La ₂ O ₃	Alpha	Ultrapure
MgO	Alpha	impurities < 55 ppm

impregnation, the samples were dried overnight in air at 40°C, then reduced in flowing H₂ on heating in 50°C steps (30 minutes) to 400°C and holding at this temperature for 16 hours. Prior to reaction, the TiO₂-supported catalysts were again reduced in flowing H₂ at 500°C for 3 hours. The rest of the supported and promoted catalysts were reduced at 400°C for 3 hours. The average metal particle sizes for these catalysts were determined by x-ray diffraction using a MoK α radiation source, hydrogen temperature programmed desorption (TPD), and static hydrogen chemisorption.

The X-ray diffraction method utilized for the determination of the average metal particle size was diffraction line broadening. The average particle size d can be determined by Scherrer equation:

$$d = K \lambda / B \cos \theta$$

where B is the broadening of the diffraction line measured at half-maximum and K is a constant of value 0.9 if a spherical particle is assumed. λ is the wavelength of the applied X-ray ($\lambda = 0.70926$ Å for a MoK α source), and θ is the Bragg angle of diffraction.

Hydrogen TPD was operated at a heating rate of 40°C/min from room temperature to 425°C using a Ar flow rate of 100 cc/min. The amount of hydrogen adsorbed was calculated based on the area under the TPD curve. Static hydrogen chemisorption measurements were made in a conventional gas volumetric system at room temperature. In this study, the metal surface areas were calculated from either hydrogen

TPD or static hydrogen chemisorption measurements, assuming a stoichiometry of $H_{1rr}/\text{Metal Atom} = 1$. The average metal particle size was calculated using the relationship $d = 5/s\rho$, (assuming particles are cubic with five sides exposed to gas phase) where d is diameter of particle, ρ is the density of the metal, and s is the metal surface area per gram of metal.

2.2 CO Hydrogenation Studies

A schematic of the reaction system used for these studies is described in Figure 2-1. The gases used for these reaction studies were obtained from Air Products and included H_2 (UHP, 99.995%), He (UPS, 99.998%), and CO (UHP, 99.8%), which were purified by passing through molecular sieve traps to remove water. Prior to passage through the molecular sieve trap, the hydrogen was passed through a Deoxo unit to remove oxygen as water.

The reaction temperature, pressure, and reactant flows were controlled by an Apple II computer. A Cyborg Isaac 91A served as the interface between the computer and 3 mass flow control meters (Brooks 5850) for controlling H_2 , CO, and He flow, a relay (Grayhill, Inc.) for controlling the reaction temperature, and a Brooks flow control valve for the reactor pressure control. A computer program was used to control flow rate, reaction temperature, and reaction pressure and is presented in Appendix A. The reactor effluent was analyzed by an on-line Perkin-Elmer Sigma 1B Gas Chromatograph. The products was separated using a porapak Q column in series with a 80/100 carbopak

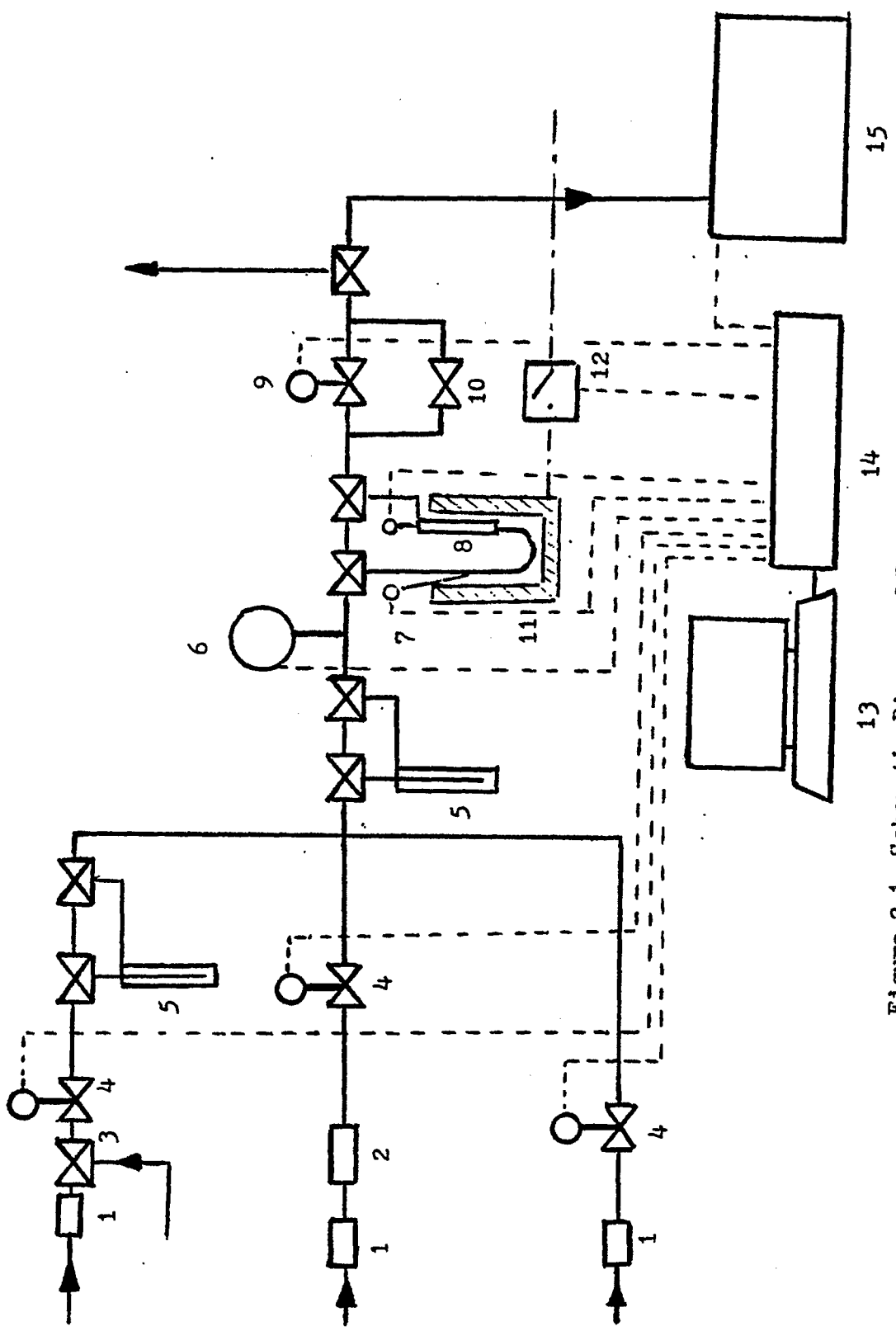


Figure 2-1 Schematic Diagram of Reactor System

1. molecular sieve trap
2. deoxo unit
3. 3-way valve
4. Brooks 5850 mass flow controller
5. saturator
6. pressure transmitter
7. thermocouple
8. differential reactor
9. pressure controller
10. needle valve
11. oven
12. relay
13. Apple II plus computer
14. Isaac 91A interface
15. gas chromatographic system

C/0.2% carbowax 1500 column. A He carrier flow rate of 20 cc/min was also utilized. The GC columns were initially held at 40°C for 2 minutes and then temperature programmed at 15°C/min to 160°C, permitting a good on-line separation of all C₁-C₆ paraffins and olefins, C₁-C₄ alcohols, C₁-C₄ aldehydes, acetone, ethyl acetate, and acetic acid in a 60 minute analysis.

The reaction study was carried out in a differential reactor at 250-300°K and 1-10 atm with H₂/CO = 1 or 0.5. High space velocities of 1,100 to 11,000 hr⁻¹ were used to keep CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. A detailed error analysis of kinetic measurements is presented in Appendix B.

2.3 Addition of Ethylene to CO/H₂ Reactants

A small amount of ethylene (2.3-3.0 mole % of the reaction mixture) was added to the CO/H₂ reactant mixture at the end of each experiment run. The relative hydrogenation, chain incorporation, hydrocarbonylation, and hydrogenolysis activities were estimated by determination of the product distribution before, during, and after the addition of ethylene.

On the basis of the results from this technique, more information is able to be obtained about the effects of alkali promoters and supports on the specific reactions, i.e., hydrogenation, chain incorporation, CO insertion, and hydrogenolysis.

2.4 Addition of Ethanol to CO/H₂ Reactants

The reaction of ethanol added to the CO/H₂ reactants was studied in a similar way as given in the above section. By determining the changes in the rate of formation for all the products during and after the addition of ethanol, the rate of dehydration, dehydrogenation, and incorporation into higher hydrocarbons, oxygenates and other products could be estimated. The acid and base nature of the catalysts system was determined by the rate of dehydration and dehydrogenation of ethanol during the addition of ethanol.⁽⁷⁰⁾

2.5 Addition of Acetaldehyde to CO/H₂ Reactants

The rate of hydrogenation, decomposition, and incorporation of acetaldehyde was determined by the addition of acetaldehyde to CO/H₂. The effects of alkali promoters and supports on the decomposition, hydrogenation, and incorporation of acetaldehyde were delineated.

The addition of these probe molecules (i.e. ethylene, ethanol and acetaldehyde) serves as a useful tool (a) to identify the possible reaction networks occurring on these catalysts, (b) to study the interrelationship between the oxygenate synthesis and hydrocarbon synthesis, (c) to identify possible surface intermediates present during synthesis, and (d) to determine the acidity and basicity of the catalyst surfaces.

**3.0 INVESTIGATION OF MECHANISMS OF OXYGENATE AND HYDROCARBON
FORMATION OVER GROUP VIII METALS: SILICA SUPPORTED
Ni, Ru, Rh AND Pd.**

3.1 Background

Formation of oxygenated compounds, especially higher alcohols, from synthesis gas is always accompanied by a formation of hydrocarbons. Thus, it is important to study mechanisms of both hydrocarbon formation and oxygenate formation to gain a better understanding of the link between oxygenate synthesis and hydrocarbon synthesis. The formation of oxygenates and hydrocarbons from CO and H₂ appears to involve a number of elementary reaction steps such as C-O bond dissociation, H-H bond scission, C-H bond formation, O-H bond formation, and C-C bond formation.^(38,85) A number of reaction mechanisms consisting of various sequences of these elementary steps have been proposed to explain product formation during CO hydrogenation.^(1,2,7,12,16,17,20,22, 82-88)

These proposed mechanisms may be classified into two groups: chain growth via hydrocarbon intermediates and chain growth via oxygenated intermediates. Due to the complexity of the mechanism of CO hydrogenation, several reaction paths may have common intermediates.⁽³⁰⁾ Due to the difficulty in differentiating one path from another, controversy still exists with regard to the mechanism(s) of CO hydrogenation.

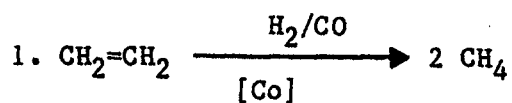
One of the effective ways for studying complex reaction mechanisms is by the addition of probe molecules to the reactant

stream during reaction. The probe molecule technique has been widely applied in heterogeneous catalysis. Applications have included (a) determining reactive intermediates, (85,86, 88-93) (b) detecting the active sites for specific reactions, (94,95) (c) determining secondary reactions of primary products, (29,96,97) (d) elucidating reaction networks in an overall reaction, (29,93,97,98) (e) determining the catalytic and chemical properties of the surface of a catalyst, (100) and (f) determining the abundance of precursors to various products under synthesis conditions. (101-106)

In order to gain a better understanding of the mechanism of CO hydrogenation, we have studied Ni/SiO₂ (a methanation catalyst), Ru/SiO₂ (a higher hydrocarbon synthesis catalyst), Rh/SiO₂ (a synthesis catalyst with a high selectivity for C₂ oxygenates), and Pd/SiO₂ (a methanol synthesis catalyst) by the addition of probe molecules to CO/H₂ under synthesis conditions. Ethylene, ethanol, and acetaldehyde were utilized as probe molecules in this study. The addition of ethylene can produce hydrocarbon intermediates, and the addition of ethanol and acetaldehyde may lead to oxygen-containing intermediates. These intermediates may be similar to those produced by Fischer-Tropsch (F-T) synthesis. The addition of such probe molecules, however, could have a great effect on the overall product distribution. The possible reactions due to the addition of these probe molecules can be summarized in Table 3-1, 3-2 and 3-3. By determining the ability of a catalyst to catalyze these specific

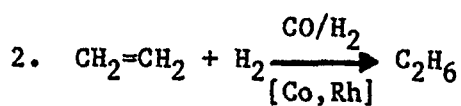
Table 3-1 Possible Reactions due to Ethylene Addition during CO Hydrogenation

Formation of CH₄



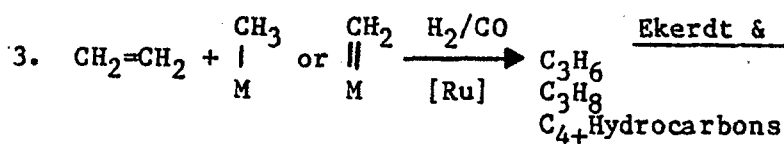
Schulz & Achtsnit (94)
van den Berg (29)

Hydrogenation



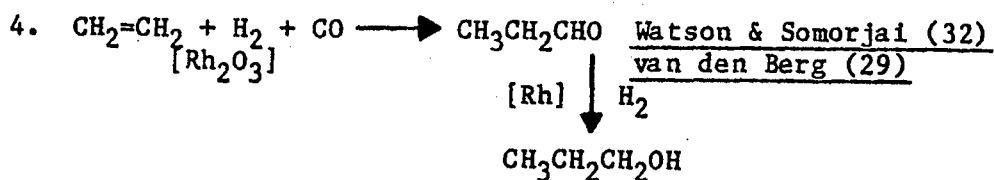
Schulz & Achtsnit (94)
van den Berg (29)

Chain Growth



Ekerdt & Bell (90)

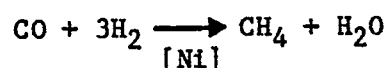
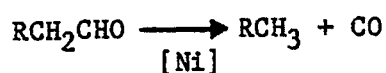
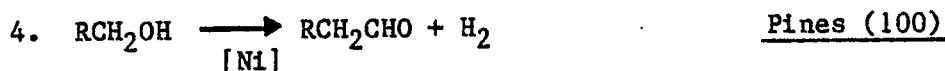
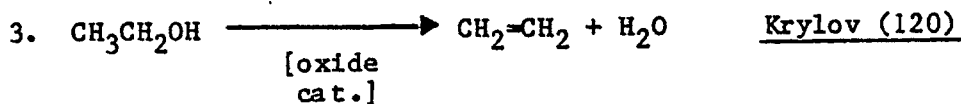
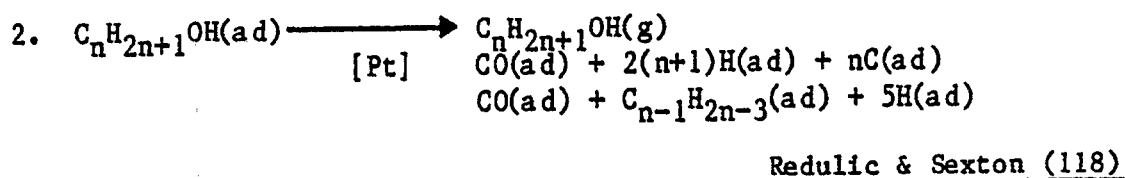
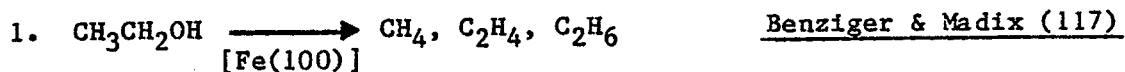
CO Insertion



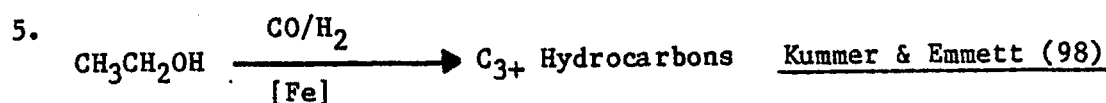
Watson & Somorjai (32)
van den Berg (29)

Table 3-2 Possible Reactions due to Ethanol Addition
During CO Hydrogenation

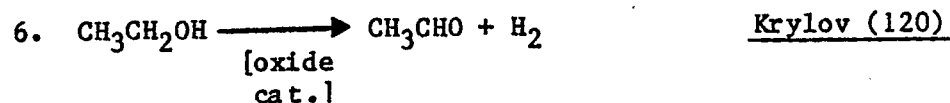
Formation of CH₄ or C₂ Hydrocarbons



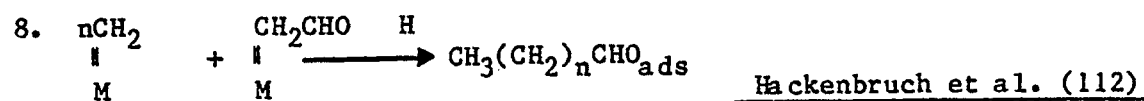
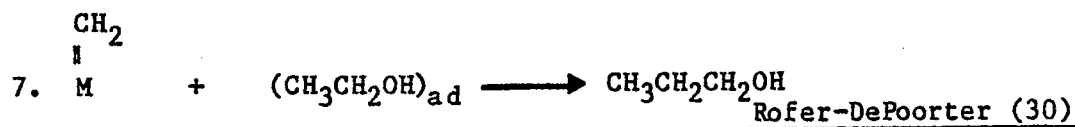
Chain Growth



Dehydrogenation



Formation of C₃ Oxygenates



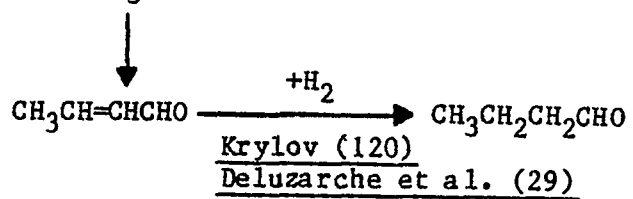
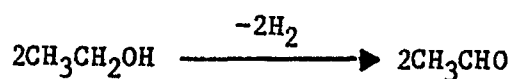
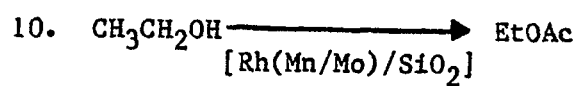
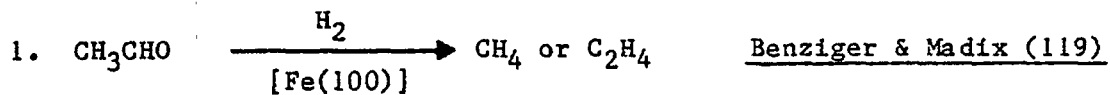
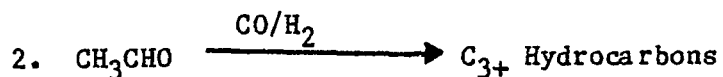
9. Formation of C₄ OxygenatesCO/H₂van den Berg (18)

Table 3-3 Possible Reactions due to Acetaldehyde Addition
During CO Hydrogenation

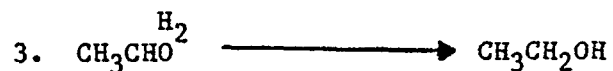
Formation of CH₄ or C₂H₄



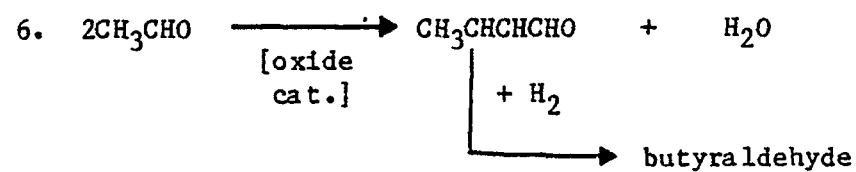
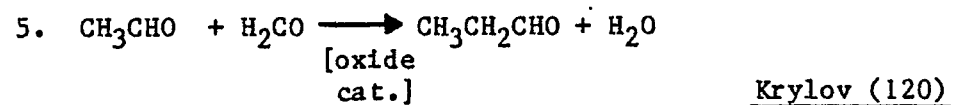
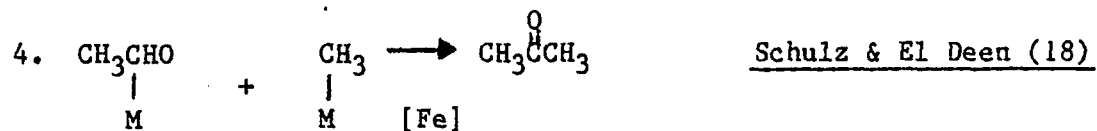
Chain Growth



Hydrogenation



Formation of C₃ Oxygenates



reaction steps, the reaction paths for the formation of hydrocarbons and oxygenates on these metal catalysts may be clarified.

3.2 Results

Metal loadings and average metal particle sizes for these catalysts are listed in Table 3-4. Due to the fact that the fraction of surface sites actually participating in certain reactions is unknown, and given the innate heterogeneity of surface sites on certain of the catalysts, only relative rates of reaction will be of concern here. Thus, the rates of reaction will be reported in units of moles/kg/hr.

3.2.1 CO Hydrogenation

The product distributions from CO hydrogenation over Ni/SiO₂, Ru/SiO₂, Rh/SiO₂, and Pd/SiO₂ are listed in Table 3-5. Ni/SiO₂ produced mainly methane with small amounts of C₂₊ hydrocarbons and oxygenates. Although Ni is a well known methanation catalyst, the formation of small quantities of oxygenated compounds is not surprising. Promoted and supported Ni catalysts are known to produce a certain amount of oxygenated compounds at 150-350°C and 1-30 atm.⁽¹⁰⁷⁾ Ru/SiO₂ showed the highest selectivity to C₂₊ hydrocarbons among these catalysts. Ruthenium is known to be one of the most active catalysts for the F-T synthesis.^(108,109) Numerous studies have reported that supported Ru catalysts, including Ru/SiO₂, are able to produce significant amounts of higher hydrocarbons.^(17,108,109)

Table 3-4 Metal Particle Size of Ni/SiO₂, Ru/SiO₂
Rh/SiO₂ and Pd/SiO₂

Catalysts	Average Metal Particle Diameter
	(A)
20 wt% Ni/SiO ₂	75 ^a 80 ^b
1.8 wt% Ru/SiO ₂	< 16 ^c < 30 ^b
3 wt% Rh/SiO ₂	< 30 ^b
2.3 wt% Pd/SiO ₂	42 ^c

^a measured by hydrogen flow chemisorption at 25°C.

^b determined by x-ray diffraction.

^c determined by static hydrogen chemisorption at 25°C, $H_{irr}/M = 1$.

Table 3-5 Activity and Product Selectivity (mol. %) during CO Hydrogenation

	20 wt% Ni/SiO ₂	1.8 wt% Ru/SiO ₂	3 wt% Rh/SiO ₂	2.3 wt% Pd/SiO ₂
r _{CO} (moles/kg/hr)	0.91	5.06	1.3	2.7
% CO Conv.	0.16	3.4	0.88	0.5
CH ₄	82.8	76.5	41.2	0.9
C ₂	12.8	8.5	6.8	1.4
C ₃₊ HC	3.7	12.6	1.8	0.4
MeOH	0	1.1	1.4	97.0
EtOH	0	0.6	18.1	0
MeCHO	0.51	0.4	13.3	0
C ₃ OX	0.14	0.3	16.6	0.14
Acetone				
Butyraldehyde	0.03	0	0.6	0
EtOAc				

(300°C, 10 atm, CO/H₂ = 1)

OX: Oxygenated Compounds

HC: Hydrocarbons

Rh/SiO₂ exhibited a good selectivity to C₂₊ oxygenated compounds with the production of only a small amount of methanol. Pd/SiO₂ showed a high selectivity for the formation of methanol. These results for Rh and Pd catalysts parallel those reported in the literature. (29,31,110,111)

3.2.2 Addition of Ethylene to CO/H₂

The addition of ethylene to CO/H₂ resulted in a significant variation in the rate of the formation of certain products and in the conversion of CO. When ethylene addition was terminated, the rates of product formation and CO conversion were essentially returned to those in existence before ethylene addition. Table 3-6 summarizes the increases in the rates of product formation as a result of ethylene addition.

Ni/SiO₂ appeared to demonstrate a moderate activity for the hydrogenolysis of ethylene to methane under synthesis conditions, while Ru/SiO₂, Rh/SiO₂, and Pd/SiO₂ were essentially not active for hydrogenolysis. The low hydrogenolysis activities of these catalysts are known to be due to the presence of adsorbed CO and competing reactions such as hydrogenation and CO insertion. (29,94) CO on metals is known to affect both hydrogenolysis and hydrogenation, (94) and it appears to have a stronger effect on hydrogenolysis than hydrogenation. Although Rh has long been known to be one of the most active catalysts for ethylene hydrogenation, (113) the selectivity for ethane was somewhat lower over Rh than over any of the other three

Table 3-6 Product Selectivity (mol. %) from Ethylene Reaction During CO Hydrogenation

	20 wt% Ni/SiO ₂	1.8 wt% Ru/SiO ₂	3 wt% Rh/SiO ₂	2.3 wt% Pd/SiO ₂
Selectivity (mol%)				
CH ₄	5	0	0	0
C ₂ H ₆	90	97.2	76	99.5
C ₃₊ HC	1	2.0	0.3	0.3
MeOH	0	0	0	(b)
C ₃ OX	3.1	0.7	23.4	0.3
r _{CO} ^(a) (w/o)	(0.91)	(4.94)	(1.3)	(2.70)
w	1.19	4.98	2.85	1.75
% C ₂ ⁼ added	1.1%	2.8%	3.1%	3.3%
r _{C₂} ^(a)	8.65	8.12	6.49	36.2
% C ₂ ⁼ conv.	75%	99%	71%	99%

(300°C, 10 atm, CO/H₂ = 1)

(a) all rates expressed as moles/kg/hr

(b) 44% decrease in overall MeOH formation

(w/o): rate of CO conversion without the addition of ethylene

w: rate of CO conversion during the addition of ethylene

catalysts. This can be readily understood by the fact that the CO insertion reaction to form C₃ oxygenated compounds (propionaldehyde and 1-propanol) competes with hydrogenation to form ethane over Rh/SiO₂ catalysts. The selectivity for CO insertion into adsorbed ethylene over these catalysts decreased in the order: Rh >> Ni > Ru > Pd. Although the abilities of these catalysts to catalyze CO insertion are different from one another, it is important to note that CO insertion would appear to be possible on all of these catalysts to a certain extent.

It is interesting to note that the addition of ethylene to CO/H₂ over Pd/SiO₂ resulted in dramatic decreases in the conversion of CO and in the formation of methanol. In contrast, a slight increase in CO conversion was observed for Ni/SiO₂ and Ru/SiO₂, and a noticeable increase in CO conversion was found for Rh/SiO₂ during the addition of ethylene to CO/H₂.

3.2.3 Addition of Ethanol to CO/H₂

The product distributions resulting from the added ethanol were estimated by a similar approach as used in the ethylene addition study. The amount of added ethanol for Ru/SiO₂ was somewhat higher compared with the other cases (Table 3-7). The concentration of ethanol is known to affect its selectivity to diethyl ether, a compound, however, not stable at temperatures above 190°C.⁽¹⁰⁰⁾ As shown in Table 3-7, Ru showed a strong activity and a high selectivity for the conversion of ethanol to C₁ and C₂ hydrocarbons as well as the

Table 3-7 Product Selectivity (mol. %) from Ethanol Reaction during CO Hydrogenation

	20 wt% Ni/SiO ₂	1.8 wt% Ru/SiO ₂	3 wt% Rh/SiO ₂	2.3 wt% Pd/SiO ₂
Selectivity (mol%)				
CH ₄	0	74.6	15.1	0.7
C ₂	0	10	2.1	4.2
C ₃₊ HC	1.8	13.2	3.0	3.3
MeOH	0	0.5	6	0 ^(b)
MeCHO	91	1.4	20.8	87.6
C ₃ OX	3.7	0	38.6	2.6
Butyral- dehyde	3.1	0	0	2
EtOAc	0	0.2	14	0
r _{CO} ^(a) (w/o)	(0.99)	(4.9)	(1.10)	(1.24)
w	0.81	4.6	1.24	1.67
% EtOH added	0.75	2.5	0.65	0.85
r _{EtOH} ^(a)	0.16	6.5	0.28	0.54
% EtOH conv.	2	81.9	16	6

(300°C, 10 atm, CO/H₂ = 1)

(a) all rates expressed as moles/kg/hr

(b) no decrease in MeOH formation

(w/o): rate of CO conversion without the addition of ethanol

w: rate of CO conversion during the addition of ethanol

apparent incorporation of ethanol into C_{3+} hydrocarbons. Rh exhibited a moderate selectivity for the conversion of ethanol to C_1 and C_2 hydrocarbons but a relatively high selectivity for the incorporation of ethanol into C_3 oxygenated compounds. In contrast to Rh and Ru, both Ni and Pd showed low selectivities for conversion or incorporation of ethanol to other products and exhibited mainly dehydrogenation activity.

3.2.4 Addition of Acetaldehyde to CO/H_2

The product distributions and rates of acetaldehyde conversion during the addition of acetaldehyde to CO/H_2 are shown in Table 3-8. In the case of Ni/SiO_2 , the selectivity for butyraldehyde was higher than that for C_3 oxygenated compounds indicating that the aldol condensation of acetaldehyde occurred on Ni/SiO_2 during the addition of acetaldehyde to CO/H_2 . In addition to the aldol condensation, Ni/SiO_2 also showed a fair selectivity for the decarbonylation of acetaldehyde to CH_4 and a high selectivity for the hydrogenation of acetaldehyde to ethanol. In contrast to Ni/SiO_2 , Ru/SiO_2 and Rh/SiO_2 did not show aldol condensation activity. Rh/SiO_2 exhibited a strong activity for the hydrogenation of acetaldehyde to ethanol. Ru/SiO_2 demonstrated a high activity in the decarbonylation of acetaldehyde to CH_4 and the conversion of acetaldehyde to C_2 hydrocarbons as well as the incorporation of acetaldehyde into C_{3+} hydrocarbons.

Table 3-8 Product Selectivity (mol. %) from Acetaldehyde Reaction During CO Hydrogenation

	20 wt% Ni/SiO ₂	1.8 wt% Ru/SiO ₂	3 wt% Rh/SiO ₂
Selectivity (mol%)			
CH ₄	13	60.7	4.8
C ₂	1.1	10.0	0.3
C ₃₊ HC	4.3	9.6	3.2
MeOH	0	0	0
EtOH	68	19.1	86
C ₃ OX	1.8	0.2	2.2
Acetone	0.4	0.26	1.1
Butyral- dehyde	10	0	0.6
EtOAc	0	0.1	0.6
$r_{CO}^{(a)}$ (w/o)	(0.68)	(4.9)	(1.32)
w	1.39	3.0	1.32
% HAc added	0.87	2.4	0.73
$r_A^{(a)}$	4.4	6.7	1.56
% HAc conv.	46	95.3	73

300°C, 10 atm, CO/H₂ = 1)

(a) all rates expressed as moles/kg/hr

(w/o) : rate of CO conversion without the addition of acetaldehyde

w : rate of CO conversion during the addition of acetaldehyde

HAc : Acetaldehyde

3.3 Discussion

3.3.1 Addition of Ethylene to CO/H₂

The added probe molecules may react with adsorbed CO, H, and/or reactive intermediates produced by CO hydrogenation and they may even block the active sites for specific reaction steps. This could result in variations in the rates of CO conversion and product formation from CO hydrogenation during the addition of probe molecules. The selectivity of probe molecule reactions in this study may be influenced by the surface concentrations of CO hydrogenation intermediates and probe molecule intermediates as well as by the capability of the catalysts to catalyze the specific reaction steps of these intermediates. As shown in Table 3-1, the adsorbed ethylene species may react with adsorbed CO and adsorbed H to form propionaldehyde and 1-propanol, may react with H to form ethane, may incorporate with CH_x to form higher hydrocarbons, or may undergo hydrogenolysis to form methane. Among these three reactants (CO, H₂, and C₂H₄), adsorbed CO and adsorbed H are probably the most abundant species on the surface even in the presence of C₂H₄. As a consequence, there may be a sufficient amount of adsorbed H and CO for hydrogenation, hydrogenolysis, or incorporation of ethylene as well as for hydrogenation of CO. Since the formation of methane and C₃+ hydrocarbons over Pd/SiO₂ is only slightly affected by the addition of ethylene to CO/H₂, the decrease in CO conversion and methanol formation would appear to be due to blockage of methanol formation

sites by the added ethylene. In contrast to Pd/SiO₂, an increase in CO conversion during the addition of ethylene to CO/H₂ was observed for Ni/SiO₂, Ru/SiO₂ and Rh/SiO₂. This appears to be due to the reaction of ethylene with adsorbed CO.⁽¹¹²⁾

All group VIII metals are known to be active in catalyzing both CO hydrogenation and ethylene hydrogenation,^(17,113) both involving C-H bond formation. They also involve different reaction steps and active site requirements,^(17,113) so that the activity for ethylene hydrogenation does not parallel that of CO hydrogenation over these metals.

As shown in Table 3-6, hydrogenolysis of ethylene only occurred on the Ni/SiO₂ catalyst. A similar observation has been reported by van Barneveld.⁽⁸⁵⁾

The capability of group VIII metals to dissociate CO has been well established in the literature.^(21,114) CO dissociation activity decreases in the order: Ni/SiO₂ > Ru/SiO₂ > Rh/SiO₂ > Pd/SiO₂. Thus, the surface concentration of nondissociatively adsorbed CO during synthesis may increase in the reverse order. Since nondissociatively adsorbed CO is known to be the precursor for insertion into adsorbed ethylene species to form C₃ oxygenates (propionaldehyde and propanol),^(32,96) the low selectivity of ethylene toward C₃ oxygenates over Pd/SiO₂ must be attributed to a lower activity of Pd to catalyze CO insertion than hydrogenation. In contrast to Pd, Rh has a greater tendency to dissociate CO. It also is the best catalyst for the formation of C₃ oxygenates from ethylene. It is likely that the

selectivity for the conversion of ethylene to C_3 oxygenates is dependent upon both the activity of the catalyst for CO insertion and the surface concentration of nondissociatively adsorbed CO.

All these metal catalysts showed very low selectivities for the incorporation of ethylene into higher hydrocarbons (Table 3-6). A similar observation has also been reported by van Barneveld.⁽⁸⁵⁾ The low selectivity for incorporation of ethylene into higher hydrocarbons could be due to the high activity of these catalysts for ethylene hydrogenation. Among Group VIII metals, only cobalt has been observed to be very active in the incorporation of ethylene into higher hydrocarbons.^(88,116)

3.3.2 Addition of Ethanol to CO/H_2

Adsorbed ethanol has been identified in the form of an ethoxy group on Fe⁽¹¹⁷⁾ and Pt,⁽¹¹⁸⁾ and it can react to produce CH_4 and C_2H_4 . In the presence of CO/H_2 , the adsorbed ethanol and its decomposition products may react with CO hydrogenation intermediates resulting in a variety of products (Table 3-2). As shown in Table 3-7, both Ni/SiO₂ and Pd/SiO₂ are active in catalyzing dehydrogenation of ethanol to acetaldehyde but inactive in catalyzing any incorporation of the ethanol into higher hydrocarbons or oxygenated compounds. Although these two metals have different CO dissociation abilities, they have similar selectivities for the incorporation and the conversion of ethanol. This could be due to the fact that different active sites are responsible for the reactions of these two

molecules. CO dissociation has been shown to take place on ensemble sites of metals,⁽¹⁷⁾ while the breaking of the C-O bond of ethanol has been proposed to require both intrinsic acidic sites and intrinsic basic sites of metals.⁽¹⁰⁰⁾

In the case of Ru, a moderate selectivity for the incorporation of ethanol into higher hydrocarbons and a high selectivity for the conversion of ethanol to C₁ and C₂ hydrocarbons were observed. As with Fe,^(97,98) Ru also shows a higher selectivity for the incorporation of ethanol into higher hydrocarbons compared with the incorporation of ethylene into higher hydrocarbons. Emmett and coworkers^(97,98) suggested that dehydration products of ethanol serve as intermediates for chain growth. However, the selectivity for the incorporation of ethylene, a dehydration product of ethanol, to C₃₊ hydrocarbons has been observed to be very low for both of these metal catalysts. The formation of a significant amount of C₃ oxygenated compounds (propanol and propionaldehyde) during the addition of ethanol to CO/H₂ over Rh/SiO₂ may be also explained by dehydration of ethanol followed by CO insertion. Reactions 7 and 8 of Table 3-2 are also possible on these metal catalysts, but there is no definite evidence for these reactions.

3.3.3. Addition of Acetaldehyde to CO/H₂

Adsorbed acetaldehyde has been found to readily form ethoxy intermediates on Fe.⁽¹¹⁹⁾ Since ethanol can dehydrogenate to form ethoxy intermediates and acetaldehyde, and acetaldehyde can

hydrogenate to form ethoxy intermediates and ethanol, the differences in product selectivity for ethanol reaction versus acetaldehyde reaction over these catalysts may relate to the relative ease of hydrogenation and dehydrogenation. If this is the case, it would not be expected that such a significant variation in CO conversion would occur during the addition of acetaldehyde to CO/H₂ as happened over Ni/SiO₂ and Ru/SiO₂. In contrast, the addition of ethanol to CO/H₂ did not produce such a change. It is not clear how adsorbed acetaldehyde modify CO hydrogenation over these two catalysts.

Ru appears to have a greater activity for the decarbonylation of adsorbed acetaldehyde intermediates than for hydrogenation of these intermediates to ethanol. Significant activity for the aldol condensation of acetaldehyde was only observed for Ni/SiO₂. Aldehydes have a great tendency to undergo the aldol condensation but it is not clear why this occurs mostly on the Ni/SiO₂ catalysts.

A small amount of acetone was observed during the addition of acetaldehyde to CO/H₂ over Ni/SiO₂, Ru/SiO₂, and Rh/SiO₂. This could proceed through dehydrogenation of the acetaldehyde to acyl intermediates followed by their association with CH₃ species to produce acetone.^(18,115) In fact, by isotopic tracing experiments, this latter step has already been shown to occur.⁽¹¹⁵⁾

3.3.4 Reaction Mechanisms

The selectivities for the various probe molecule reactions are summarized in Table 3-9. Ni/SiO₂, Ru/SiO₂, Rh/SiO₂ and Pd/SiO₂

Table 3-9 Selectivities of the Probe Molecule Reactions

	Ni/SiO ₂	Ru/SiO ₂	Rh/SiO ₂	Pd/SiO ₂
CO Dissociation ^(38,39)	+++	+++	++	0
Hydrogenation of C ₂ ⁼	+++	+++	+++	+++
Hydrogenolysis of C ₂ ⁼	+	0	0	0
Incorporation of C ₂ ⁼ into C ₃₊ HC	+	+	0	0
CO insertion in C ₂ ⁼	+	0	+++	0
Dehydrogenation of EtOH	+++	+	+++	+++
Dehydration of EtOH	0	++	+	+
Conversion of EtOH to to CH ₄	0	+++	+++	0
Conversion of EtOH into C ₃₊ OX	+	0	+++	+
Conversion of EtOH into C ₃₊ HC	+	+++	+	+
Conversion of MeCHO into C ₃₊ OX	+	0	+	NA
Conversion of MeCHO into C ₃₊ HC	+	++	+	NA
Decarbonylation of MeCHO	+++	+++	+	NA
Aldol Condensation	++	0	0	NA

(300°C, 10 atm, CO/H₂ = 1)

+++ : strong (> 10% of probe reactant incorporated)

++ : moderate (> 5%)

+ : weak (> 1%)

0 : inactive (< 1%)

catalysts demonstrated differences not only in product selectivity for CO hydrogenation but also in their catalytic capabilities for hydrogenation, hydrogenolysis, dehydrogenation, CO insertion, and the incorporation of ethylene, ethanol and acetaldehyde during CO hydrogenation. The reaction steps suggested by the results of this study and by those reported in the literature⁽⁸²⁻¹¹²⁾ are summarized in Figure 3-1. Ni, a methanation catalyst, showed a strong catalytic activity for ethylene hydrogenation, ethylene hydrogenolysis, ethanol dehydrogenation, and acetaldehyde hydrogenation but poor catalytic activity for CO insertion and incorporation of ethylene, ethanol, or acetaldehyde into higher hydrocarbons and oxygenated compounds. The catalytic activities displayed by Ni/SiO₂ appear to be unfavorable for the formation of higher hydrocarbons and oxygenated compounds. Ru/SiO₂, a good higher hydrocarbon synthesis catalyst, demonstrated a strong catalytic activity for ethylene hydrogenation, conversion of ethanol to C₁ and C₂ hydrocarbons, decarbonylation of acetaldehyde, and incorporation of ethanol and acetaldehyde into higher hydrocarbons but a weak catalytic activity for hydrogenolysis of ethylene and CO insertion. A poor CO insertion capability and a strong decarbonylation activity prevent the formation of C₂₊ oxygenated compounds, and they exclude oxygenated intermediates as major intermediates for hydrocarbon chain growth over Ru/SiO₂. Rh/SiO₂, a good C₂ oxygenate synthesis catalyst, exhibited strong catalytic activity for the incorporation of ethylene and ethanol to C₃ oxygenated compounds but poor catalytic activity for decarbonylation

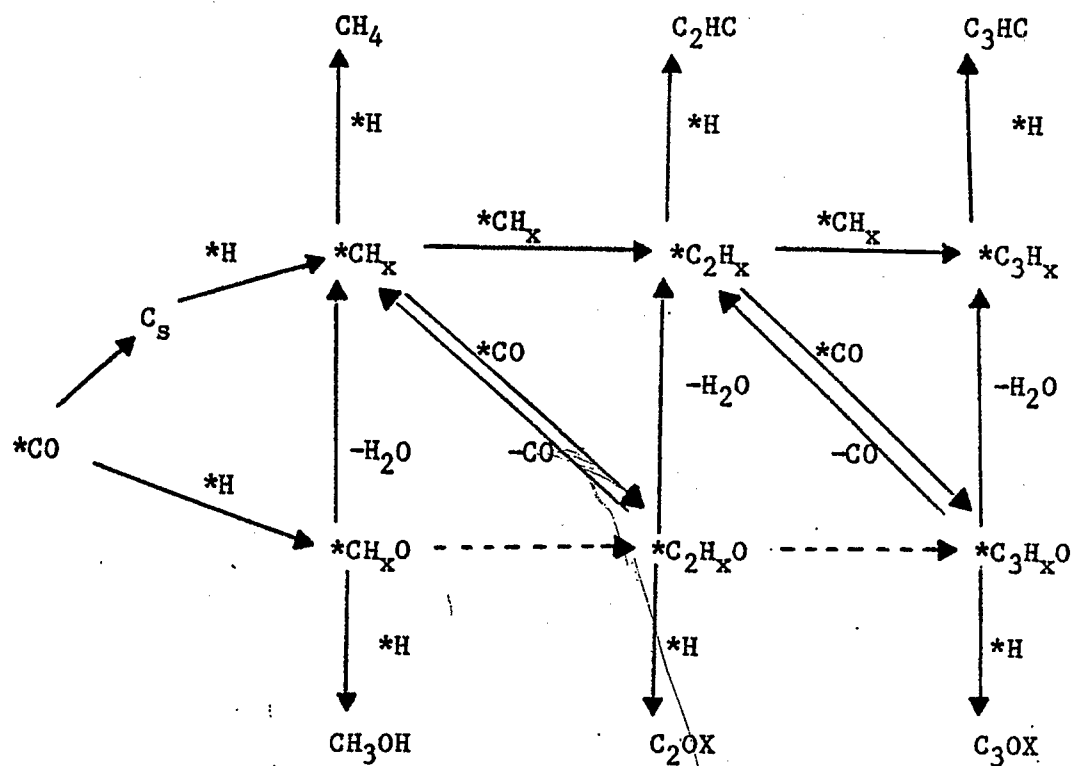


Figure 3-1 Possible Reaction Network for CO Hydrogenation

of acetaldehyde and hydrogenolysis of ethylene. A strong tendency for the incorporation of ethylene and ethanol into C_{3+} oxygenated compounds indicates that both oxygenated and hydrocarbon intermediates could be important for chain growth to form oxygenated compounds. Pd/SiO₂, a methanol synthesis catalyst, showed strong catalytic activity for hydrogenation and poor catalytic activity for CO insertion, conversion of ethanol to methane, and the incorporation of ethylene and ethanol into higher hydrocarbons and oxygenated compounds. The activity in catalyzing probe molecule reactions exhibited by Pd/SiO₂ is somewhat similar to those displayed by Ni/SiO₂. They do not favor the formation of C_{2+} species.

3.4 Conclusions

The synthesis of oxygenated compounds and hydrocarbons over Ni/SiO₂, Ru/SiO₂, Rh/SiO₂, and Pd/SiO₂ would appear to follow different reaction paths resulting in different product distributions at 10 atm. The formation of C_{2+} oxygenated compounds over Rh/SiO₂ is controlled by both the activity of the catalyst to catalyze CO insertion and the surface concentration of nondissociatively adsorbed CO. Both oxygenated and hydrocarbon intermediates may be important for oxygenate chain growth on Rh. The insertion of CH_x into C_yH_x appears to be a major route for the formation of higher hydrocarbons over Ru/SiO₂. The inability of Ni/SiO₂ and Pd/SiO₂ to catalyze the formation of C_{2+} species would seem to be related to their poor abilities in catalyzing the incorporation of hydrocarbon and

oxygenated intermediates to form C_{2+} species. Nevertheless, the factors for controlling these specific reaction steps remain as yet unclear. A more thorough study of the relationship between the surface states and electronic configuration of these metals and their catalytic abilities for specific reaction steps (as shown in Figure 3-1) should provide a deeper insight into the mechanism of product formation over the Group VIII metals.

4.0 SUPPORT EFFECT ON OXYGENATE SYNTHESIS OVER Rh CATALYSTS

4.1 Background

Support compositions are known to have a great effect⁽¹⁻¹²⁾ on the performance of group VIII metal catalysts, especially rhodium catalysts. Depending on the support composition and pretreatment conditions, Rh catalysts can produce a wide range of oxygenated compounds and hydrocarbons including methanol, higher alcohols, aldehydes, acids, esters, methane, and higher hydrocarbons.^{(6,10-12,}

62) Rh on MgO was found to exhibit a 90% selectivity to methanol.⁽⁶⁾ Use of Al₂O₃ resulted mainly in CH₄ formation while use of SiO₂, TiO₂, or CeO₂ produced both alcohols and hydrocarbons.⁽⁶⁾ It is apparent that the active sites for the formation of this variety of products are greatly affected by metal-support interactions. Various mechanisms for the effect of the support on oxygenate synthesis have been proposed. Katzer et al.⁽⁶⁾ have suggested that Rh on MgO, a basic support which has an electron donating capability, would perform like Pd. By the same argument, Rh on an acidic support, which would have a tendency to withdraw electrons, should behave like Ru. In contrast, Somorjai and coworkers^(32,123) have suggested that one of the major functions of an oxide support is to stabilize Rh cations which they suggested to be the active sites for oxygenate formation.

The study discussed in this chapter is aimed at expanding our current knowledge of the effect of metal-support interactions on

oxygenate synthesis and elucidating the factors which affect selectivity to oxygenates and hydrocarbons. A series of supported Rh catalysts including Al_2O_3 , SiO_2 , TiO_2 , La_2O_3 and MgO-supported catalysts and unsupported Rh black were studied by CO hydrogenation and by the addition of probe reactant molecules (ethylene, ethanol, and acetaldehyde) to the CO/H_2 reaction mixture under synthesis conditions.

4.2 Results

4.2.1 CO Hydrogenation

The rates of formation of major products as a function of time for Rh black, $\text{Rh}/\text{Al}_2\text{O}_3$, Rh/TiO_2 , $\text{Rh}/\text{La}_2\text{O}_3$, and Rh/MgO are shown in Figures 4-1, 4-2, and 4-3. Although these catalysts exhibited different patterns for the rate of product formation vs. time, all of them showed essentially a stable product selectivity after 300 minutes on stream.

The product distributions from reaction over these catalysts at 300 to 360 min time-on-stream, 300°C and 10 atm are given in Table 4-1. The selectivity for the formation of oxygenated compounds at 10 atm increased in the order: $\text{Rh}/\text{Al}_2\text{O}_3 < \text{Rh}/\text{TiO}_2 < \text{Rh}/\text{MgO} < \text{Rh}/\text{La}_2\text{O}_3 < \text{Rh}/\text{SiO}_2$. A similar trend in selectivity to oxygenated compounds was also observed for reaction at 1.3 atm (Table 4-2). High pressures appear to enhance the selectivity to C_2 oxygenated compounds over Rh/TiO_2 , Rh/SiO_2 , and Rh/MgO . The influence of pressure on

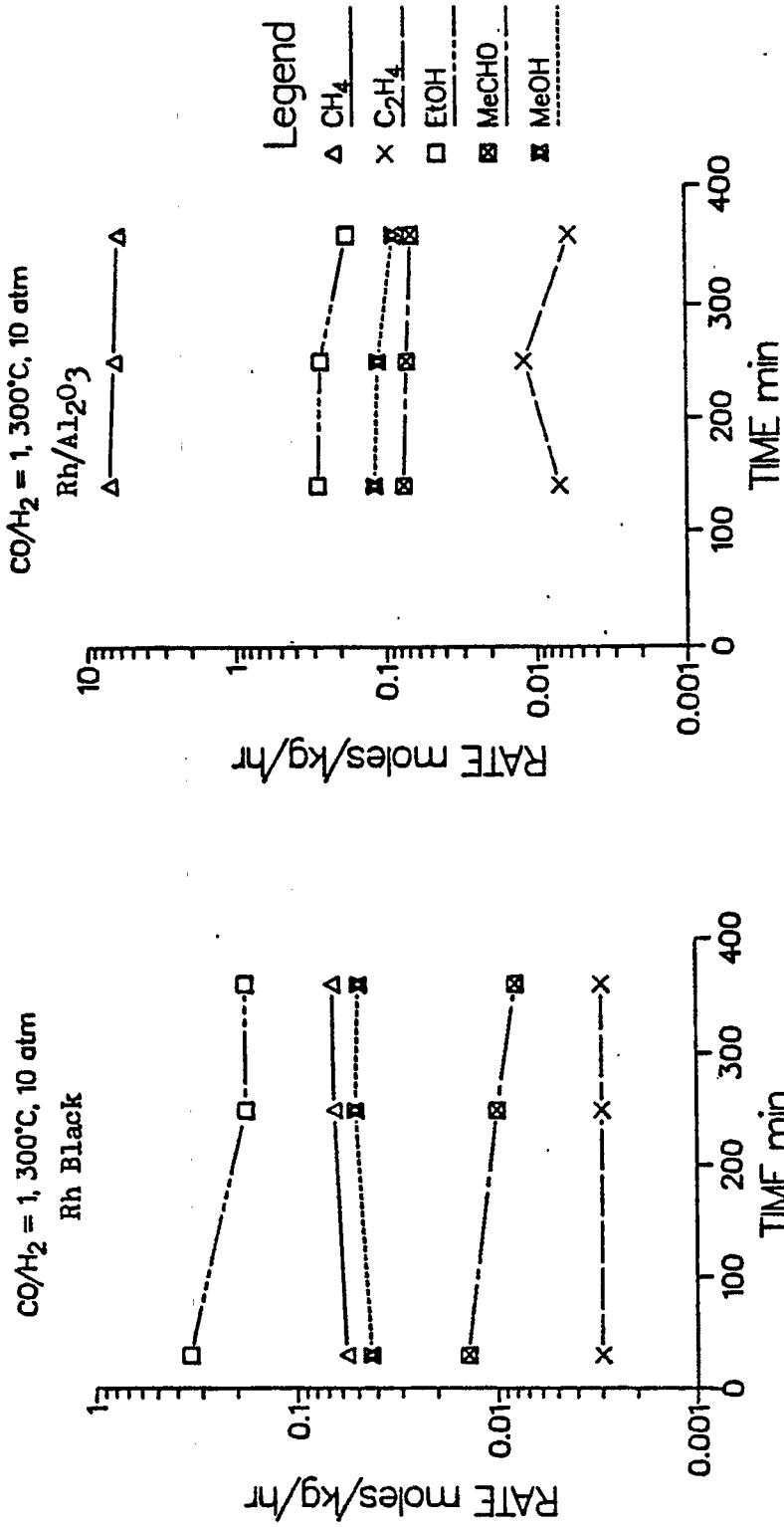


Figure 4-1 Product Formation Rate vs. Time over Rh Black and Rh/Al₂O₃

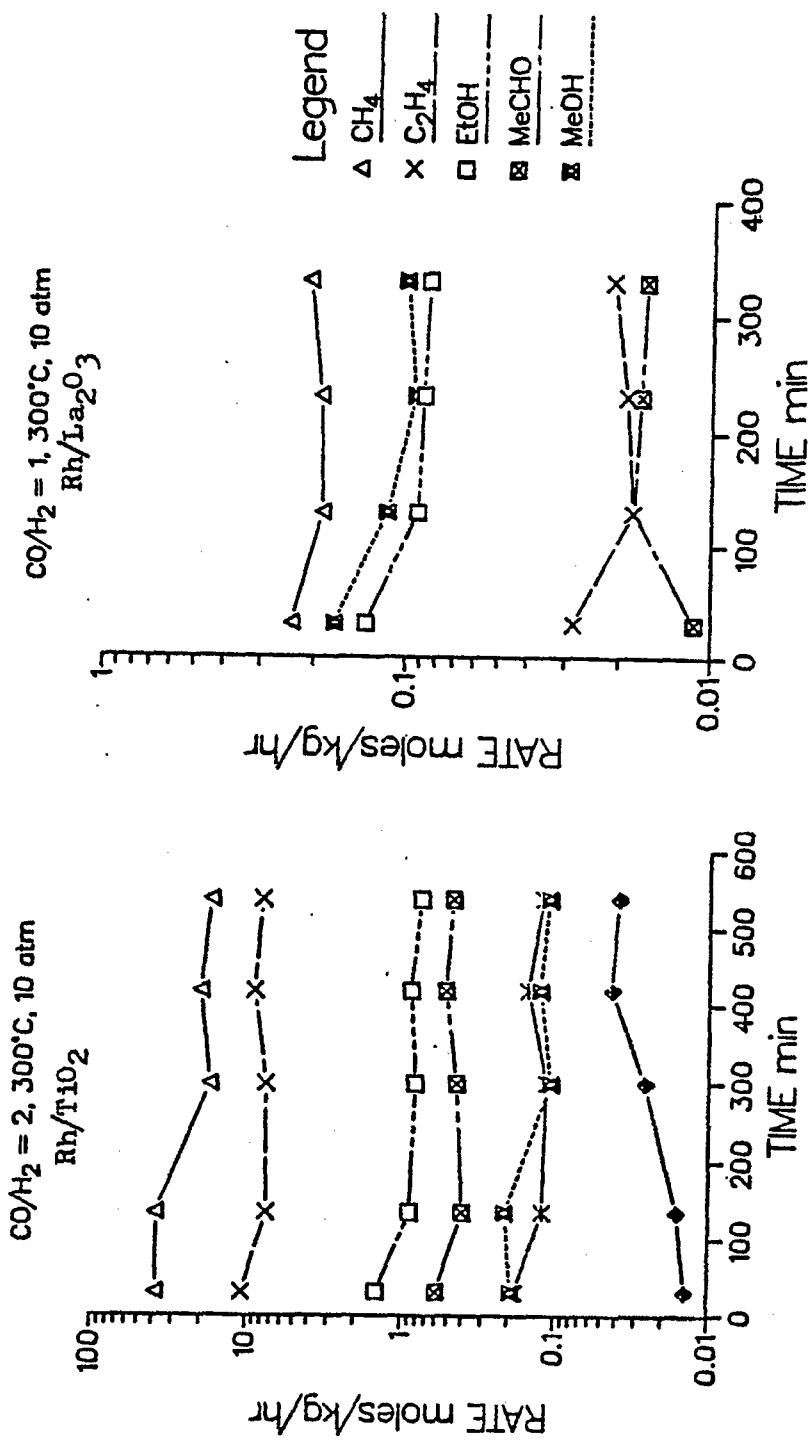


Figure 4-2 Product Formation Rate vs. Time over Rh/TiO₂ and Rh/La₂O₃

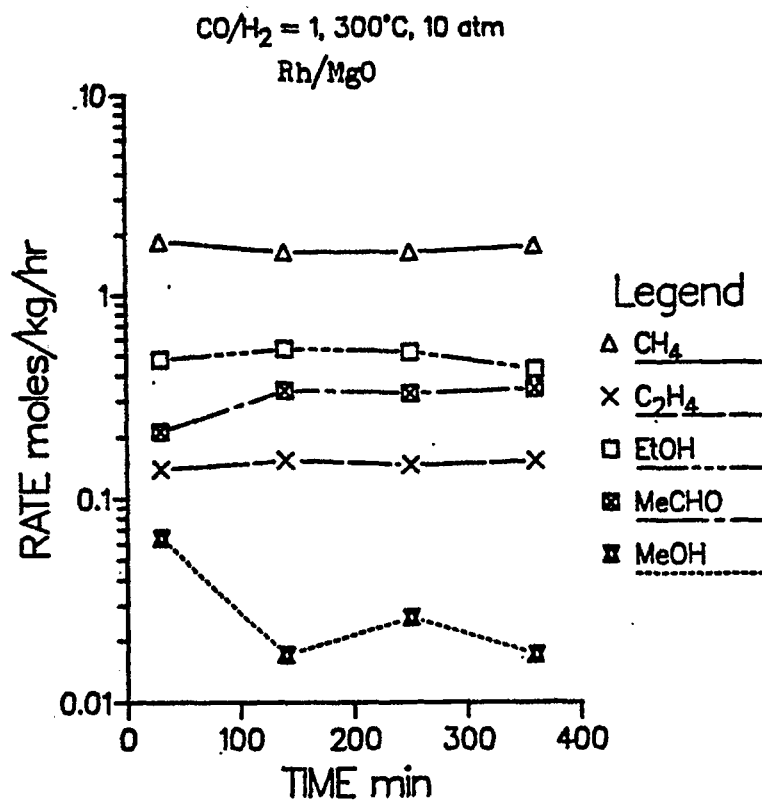


Figure 4-3 Product Formation Rate vs. Time over Rh/MgO

Table 4-1 Effect of Support on CO Hydrogenation Selectivity at 10 atm

Catalysts	Rh black	Rh/Al ₂ O ₃	Rh/TiO ₂ *	Rh/SiO ₂	a Rh/La ₂ O ₃	a Rh/MgO
% Dispersion	2	33	24	18	26	15
Rate (mole/kg/hr)	0.846	7.73	17.31	1.099	0.772	5.23
Selectivity (wt %)						
CH ₄	10.9	70.0	49.9	22.0	22.8	31.6
C ₂ +	47.3	13.7	32.4	8.0	18.9	26.8
Total OX	41.8	16.3	17.7	70.0	58.3	42.5
MeOH	15.1	2.1	0.3	1.2	21.6	.6
C ₂ OX	26.4	8.7	10.4	50.3	30.9	37.8

CO/H₂ = 1, 300°C, and 10 atm
 C₃+ O_x are included in Total OX
 *CO/H₂ = 2

Table 4-2 Effect of Support on CO Hydrogenation
Selectivity at 1.3 atm

Catalysts	Rh/TiO ₂ *	Rh/SiO ₂	Rh/La ₂ O ₃	Rh/MgO
% Dispersion	24	18	26	15
Press. atm	1.3	1.6	1.3	1.3
Rate (mole/kg/hr)	1.49	0.395	0.68	0.32
Selectivity (wt %)				
CH ₄	44.2	28.9	20.6	47.5
C ₂₊	53.8	33.2	43.5	32.0
Total OX	2	37.9	35.9	20.3
MeOH	0	1.2	1.7	1.5
C ₂ OX	2	32.2	29.5	17

CO/H₂ = 1, 300°C

GHSV = 7,000-11,000 Hr.

C₃₊ Ox are included in Total OX

*CO/H₂ = 2

selectivity over $\text{Rh}/\text{Al}_2\text{O}_3$ has also been found to be similar to that for these catalysts.⁽¹¹⁰⁾ In contrast, high pressures increase the selectivity to methanol rather than to C_2 oxygenated compounds for $\text{Rh}/\text{La}_2\text{O}_3$. It is interesting to note that Rh black shows a significant higher selectivity for the formation of oxygenated compounds compared with those reported for metallic Rh single crystals or foils.⁽¹²⁴⁾

4.2.2 Addition of Ethylene to CO/H_2

In order to determine the effect of the support on the hydrogenation and hydrocarbonylation activities of these supported Rh catalysts, a small amount of ethylene (3.3% - 3.5 mole % of C_2H_4 in CO/H_2) was added to the CO/H_2 reactant stream under synthesis conditions. As shown in Figure 4-4, the addition of ethylene to the reaction mixture over Rh/SiO_2 resulted in a significant increase in the rates of formation of ethane, propionaldehyde, and 1-propanol, while the rates of formation of methane, acetaldehyde, ethanol, and other oxygenates were essentially not affected. When ethylene addition was stopped, the activity and selectivity of the catalyst returned to those existing before ethylene addition. Similar patterns of change in product distribution during the addition of ethylene was also observed for other catalysts in this study. The increase in the rate of formation of ethane and of C_3 oxygenated compounds (propionaldehyde and 1-propanol) appeared to result from hydrogenation and hydrocarbonylation of the added ethylene, respectively. The selectivities for the reactions of added ethylene

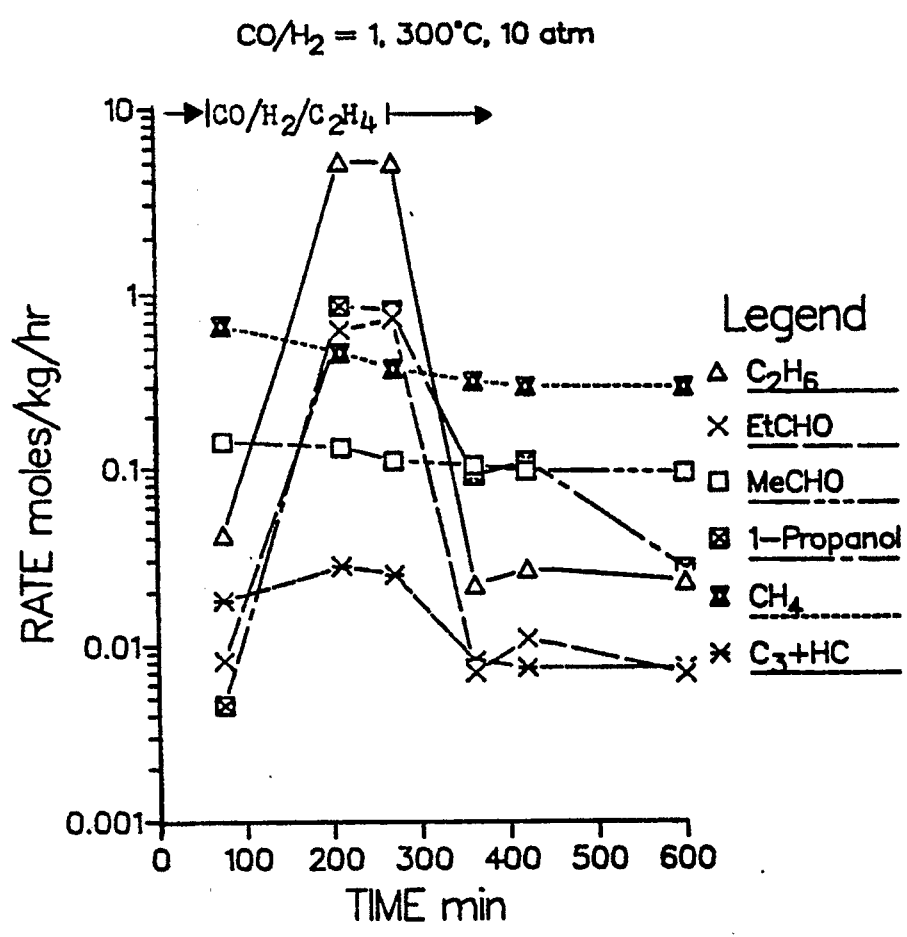


Figure 4-4 Rate of Product Formation during Addition of Ethylene to CO/H_2 over Rh/SiO_2

over variously supported Rh catalysts are summarized in Table 4-3. The low selectivity for the incorporation of ethylene into C_3+ hydrocarbons indicates that hydrogenation and hydrocarbonylation of ethylene overwhelm the incorporation of ethylene into hydrocarbon chain growth.

The results suggest that conversion of C_3 oxygenated compounds to C_3 hydrocarbons did not occur to any noticeable extent. Therefore, ethylene addition can serve as a probe for determining the relative activity of these supported catalysts for catalyzing hydrogenation and hydrocarbonylation (CO insertion) during CO hydrogenation. The selectivity for CO insertion increased in the order: $Rh/Al_2O_3 < Rh/TiO_2 < Rh/MgO$, $Rh/La_2O_3 < Rh/SiO_2$ while hydrogenation selectivity increased in the reverse order. Figure 4-5 shows a comparison of C_2 oxygenate selectivity during CO hydrogenation with C_3 oxygenate selectivity from ethylene during the addition of ethylene to CO/H_2 . The selectivities for CO insertion appear to parallel C_2 oxygenate selectivities of supported Rh catalysts during CO hydrogenation. In contrast, Rh black did not follow the trend as shown by supported Rh catalyst (see Table 4-1 and 4-3).

4.2.3 Addition of Ethanol to CO/H_2

The selectivities for reaction of added ethanol are shown in Table 4-4. The concentration of added ethanol was controlled in the range of 0.1 to 0.9%. The selectivity for dehydration decreased in the order: $Rh/Al_2O_3 > Rh \text{ black} > Rh/La_2O_3 > Rh/SiO_2 > Rh/MgO$.

Table 4-3 Product Selectivity from Ethylene Reaction during
CO Hydrogenation over Various Supported Rh Catalysts

	Rh black	Rh/Al ₂ O ₃	Rh/TiO ₂ *	Rh/SiO ₂	Rh/La ₂ O ₃	Rh/MgO
rate of C ₂ conversion	6.42	9.15	8.30	6.4	2.53	5.37
Selectivity of C ₂ H ₄ reacted mole %						
C ₂ H ₆	76.2	99.3	92.7	76.2	85.8	87.6
C ₃ OX	23.5	0.64	2.6	23.5	13.9	9.9
C ₃ +HC	0.3	0.34	4.7	0.3	0.3	2.4

300°C, CO/H₂ = 1, 10 atm

*CO/H₂ = 2

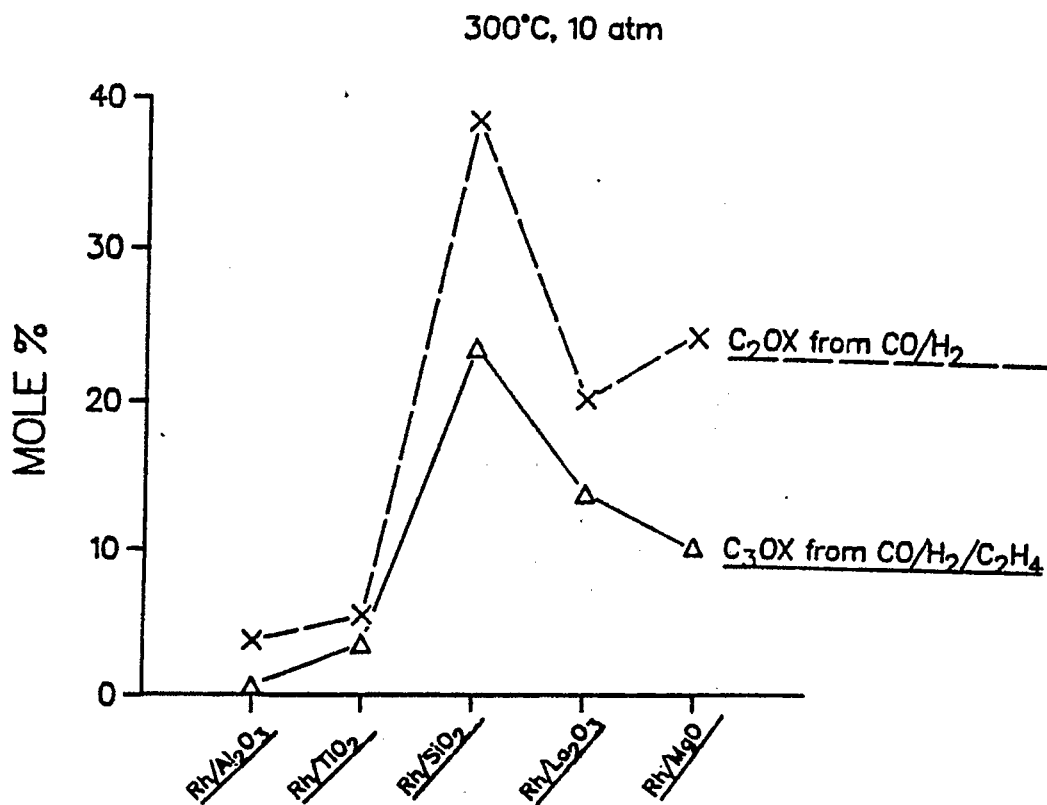


Figure 4-5 A Comparison of C₃ Oxygenate Selectivity during CO Hydrogenation with C₃ Oxygenate Selectivity during Addition of Ethylene to CO/H₂

Table 4-4 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Supported Rh Catalysts

	Rh black	Rh/Al ₂ O ₃	Rh/SiO ₂	Rh/La ₂ O ₃	Rh/MgO
Amount of EtOH Added to CO/H ₂ (%)	0.89	0.3	0.65	0.11	0.45
Rate of EtOH Conv. (mole/kg/hr)	0.116	0.12	0.28	0.27	0.095
Selectivity (mole %)					
CH ₄	0	0	15.1	84	27.2
C ₂	8.7	16.9	2.1	6	0
C ₃ +	0	16.9	3.0	9	0
MeCHO	91.3	35.5	20.8	0.5	52.4
C ₃ OX	0	3.3	38.6	0.5	20
EtOAc	0	27.1	14	0	0.4

Selectivity for dehydrogenation decreased in the order: Rh black > Rh/MgO > Rh/Al₂O₃ > Rh/SiO₂ > Rh/La₂O₃. In addition to dehydrogenation activity, Rh/SiO₂ and Rh/MgO also exhibited a relatively high selectivity for incorporation of ethanol to C₃ oxygenated compounds. The formation of ethyl acetate from ethanol was observed over Rh/Al₂O₃ and Rh/SiO₂ while this reaction step was not significant over Rh/MgO, Rh/La₂O₃ and Rh black.

4.2.4 Addition of Acetaldehyde to CO/H₂

The addition of acetaldehyde was carried out over Rh black, Rh/Al₂O₃, Rh/SiO₂ and Rh/MgO. The selectivities for reactions of the added acetaldehyde are given in Table 4-5. Rh black, Rh/MgO and Rh/Al₂O₃ exhibited high selectivities to C₂ hydrocarbons. In contrast, Rh/SiO₂ showed mainly hydrogenation activity with a weak decarbonylation activity. In addition to formation of a small amount of C₃ oxygenated compounds and hydrocarbons, acetaldehyde can also be decomposed to CO and H₂. Since an isotopic tracer study would be required to determine the rate of this reaction step, no attempt was made to determine the extent of this reaction. However, there was no significant change in the rates of formation of primary products from CO and H₂.

4.3 Discussions

Though dispersion has been suggested to be an important factor for controlling product distribution from CO hydrogenation over

Table 4-5 Product Selectivity from Acetaldehyde Reaction during
CO Hydrogenation over Supported Rh Catalysts

	Rh black	Rh/Al ₂ O ₃	Rh/SiO ₂	Rh/MgO
Amount of MeCHO added to CO/H ₂ (%)	2.2	0.5	0.73	2.2
Rate of MeCHO conversion (mole/kg/hr)	17.4	1.3	1.5	2.2
Selectivity (mole %)				
CH ₄	0.8	0	4.8	0
C ₂	83.4	50.1	0.3	72.6
C ₃ +HC	0	8.8	3.2	0
EtOH	12.9	33.2	87	18.8
C ₃ OX	2.2	0.92	2.3	0
C ₄ OX	0.3	6.8	1.2	0

supported Rh catalysts⁽¹²⁵⁾, dispersions ranging from 15 to 33 among these supported catalysts as shown in Table 4-1 should not result in such a significant variation in product distribution. It appears that metal-support interactions played an important role in modifying product distributions.

4.3.1 Effect of Reaction Pressure

An increase in reaction pressure resulted in an increase in the selectivity to C₂ oxygenated compounds for Al₂O₃, TiO₂, SiO₂ and MgO supported Rh catalysts and an enhanced selectivity to methanol for Rh/La₂O₃. This could be due to an increase in surface concentration of nondissociatively adsorbed CO.

Ramamoorthy and Gonzales⁽⁷²⁾ have demonstrated that high coverages of CO can block CO dissociation. Somorjai⁽⁷³⁾ has pointed out that at high pressures the reaction time may be longer than the period between collisions of the reactant with the surface sites of the catalyst. Thus, the adsorbed CO could act to block the ensemble of sites needed for CO dissociation longer, resulting in a higher coverage of undissociated CO at higher pressures than at lower pressures. The increase in coverage of nondissociatively adsorbed CO could enhance those reactions which require nondissociatively adsorbed CO in this manner. Methanol has been shown to be formed via the hydrogenation of nondissociatively adsorbed CO.⁽²²⁾ The formation of C₂ oxygenated compounds has also been demonstrated to involve the

insertion of nondissociatively adsorbed CO into surface CH_x species. (20,32)

Nondissociatively adsorbed CO appears to be an essential precursor for the formation of oxygenated compounds. Thus an increase in surface concentration of nondissociatively adsorbed CO should increase the selectivity to either methanol or C_{2+} oxygenated compounds. Nevertheless, the factors governing the selectivity to either methanol or C_{2+} oxygenated compounds as reaction pressure increases are still not clear. (74)

An increase in activity and selectivity for methanol formation with increasing pressure over $\text{Rh/La}_2\text{O}_3$ may be related to an involvement of active sites on La_2O_3 . La_2O_3 has been observed to be active in methanol synthesis at 250°C and 1 atm. (75) Kuznetzov et al. (75) have suggested, based on their NMR results, that CHO and CHO_2 are the precursors for the formation of methanol. On $\text{Rh/La}_2\text{O}_3$, these precursors could be formed on La_2O_3 and then hydrogenated to methanol on the Rh.

4.3.2 Effect of Support on Product Distribution

Previous results reported in Chapter 3 have suggested that the formation of C_{2+} oxygenated compounds is partially controlled by both the activity of the catalyst to catalyze CO insertion and the surface concentration of nondissociatively adsorbed CO. The difference in product distribution among these variously supported Rh catalyst as shown in Table 4-1 and 4-2 may be attributed to an effect of the

support on the activity of Rh for CO dissociation, hydrogenation, and CO insertion. The effect of the support on CO dissociation ability was found to decrease in the order: $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{MgO}$.⁽⁶⁸⁾ Strong CO dissociation activity would result in less nondissociatively adsorbed CO available for CO insertion to form C_2 oxygenated compounds. In addition to CO dissociation activity, the nature of the support also exhibited a strong effect on CO insertion ability and hydrogenation capability of the Rh catalysts. The CO insertion ability decreases in the order: $\text{Rh/SiO}_2 > \text{Rh/La}_2\text{O}_3 > \text{Rh/MgO} > \text{Rh/TiO}_2 > \text{Rh/Al}_2\text{O}_3$ while hydrogenation ability decreased in the reverse order. The trend in C_2 oxygenate selectivity appears to parallel that of CO insertion ability rather than that of CO dissociation capability. This can be understood by the fact that nondissociatively adsorbed CO is an abundant species on the catalyst surface, even on the surface of a strong CO dissociation catalyst such as Ru.⁽¹²⁶⁾ Results of ethylene addition to the CO/ H_2 reaction mixture study over these catalysts also showed that formation of C_3 oxygenated compounds from reaction of ethylene with H_2/CO did not deplete the adsorbed CO in such a way so as to affect the formation of C_2 oxygenated compounds (which have to be also formed presumably from adsorbed CO). This is another indication that abundant adsorbed CO is available for CO insertion.

Although it is still not possible to determine what type of active site is responsible for CO insertion, results of ethylene addition over Rh black have showed that the active sites for CO

insertion do not require stabilization by a promoter or by an oxide support. This is contrary to what has been suggested by Somorjai and coworkers.^(32,123)

In addition to the insertion of CO into adsorbed ethylene, C₃ oxygenated compounds can also be formed via incorporation of ethanol. Supports such as SiO₂ and MgO appear to promote this reaction step. This suggests that oxygenated intermediates are also important for oxygenate chain growth over these two catalysts. In contrast to Rh/SiO₂ and Rh/MgO, this reaction step was not observed for Rh black, Rh/La₂O₃, and Rh/Al₂O₃. This may be the reason why Rh black and Rh/SiO₂, which showed similar selectivity for CO insertion into adsorbed ethylene, exhibited different C₂ oxygenate selectivity during CO hydrogenation.

Alcohol selectivity during CO hydrogenation has been found in the past to correlate well with the acidity or basicity of the support.⁽⁶⁾ The acidity or basicity of supported Rh catalysts under synthesis conditions may be determined by the selectivity for dehydration or dehydrogenation of added ethanol. Acidity of the catalyst appears to decrease in the order: Rh/Al₂O₃ > Rh/La₂O₃ > Rh/SiO₂ > Rh/MgO. It can be seen from this study that there is no direct relationship between alcohol selectivity and the acidity/basicity of the catalysts. Many factors may contribute to the disagreement between our study and those reported by Katzer et al.⁽⁶⁾ These include catalyst preparation technique, the nature of the Rh precursor, dispersion, metal loading, source of the support,

and pretreatment conditions. This complication can be seen from one of our later studies of Rh/MgO which is reported in Chapter 9. Rh/MgO reduced at 250°C produced high yields of methanol while reduction at 400°C resulted in a high selectivity to C₂ oxygenated compounds. Similar trends in the effect of reduction on the selectivity of Rh/MgO have also been reported by Poels.⁽⁶²⁾ In fact, the acidity or basicity of the catalyst can be modified not only by the use of a support but also by the use of alkali promoters. van den Berg⁽²⁹⁾ studied CO hydrogenation over a series of Na-promoted MnMoRh/SiO₂ catalysts in order to investigate the effect of acidity or basicity of catalysts on alcohol selectivity. No correlation between selectivity and acidity or basicity of catalyst was observed.

Major products of acetaldehyde reaction on Rh black, Rh/Al₂O₃, Rh/SiO₂, and Rh/MgO are C₂ hydrocarbons and ethanol. The formation of C₂ hydrocarbons has been suggested to be via C-O bond scission of diadsorbed acetaldehyde.⁽¹¹⁹⁾ It is still not clear how the support may affect this C-O bond breaking process. The selectivity for acetaldehyde hydrogenation as shown in Table 4-5 did not parallel the selectivity for ethylene hydrogenation (Table 4-3). These results are also not consistent with the mole ratio of [CH₃CH₂OH]/[CH₃CHO] during CO hydrogenation as shown in Table 4-6. This seems to suggest that ethanol is not produced by direct hydrogenation of acetaldehyde. This argument has been supported by a recent isotope tracing study.⁽¹²⁷⁾

Table 4-6 Mole Ratio of [EtOH]/[MeCHO] during CO Hydrogenation
over Rh Catalysts

	Rh black	Rh/Al ₂ O ₃	Rh/SiO ₂	Rh/MgO
[EtOH]/[MeCHO]	7.3	3.3	2.6	2.2

4.4 Conclusions

CO insertion is an important factor for the formation of C₂₊ oxygenated compounds. This reaction step was found to be able to proceed on Rh black in the absence of either a support or a promoter. Correlations between oxygenate selectivity and acidity/basicity of catalysts was not observed. Factors affecting product distribution apparently include CO dissociation, CO insertion, hydrogenation, and incorporation of hydrocarbon and oxygenated intermediates. These factors were found to be strongly dependent upon the support composition.

5.0 EFFECT OF ALKALI PROMOTION OF Rh/TiO₂

5.1 Background

It is known that the addition of alkali salts to methanol synthesis catalysts often results in increased yields of higher alcohols. However, many questions still remain concerning the effect of various alkali species on the catalyst components and mechanism(s) of alcohol synthesis.

Rh/TiO₂ provides an excellent model system for studying the effects of alkali promoters on alcohol synthesis. It can produce significant quantities of both alcohols and hydrocarbons from the reaction of CO with H₂. Thus, one is able to simultaneously determine how both alcohol and hydrocarbon synthesis reactions are affected by the presence of a promoter. This chapter reports on an investigation of the effect of various alkali species (Li, K, and Cs) on the activity and selectivity of Rh/TiO₂ for CO hydrogenation and on the deactivation characteristics of these catalysts.

5.2 Results

5.2.1 Alkali-Promoted Rh/TiO₂

The activities of alkali-promoted and unpromoted Rh/TiO₂ for CO conversion as a function of time are shown in Figure 5-1. An expression of activity in moles/kg/hr has been used due to the uncertainty in the estimation of the number of Rh surface atoms as a

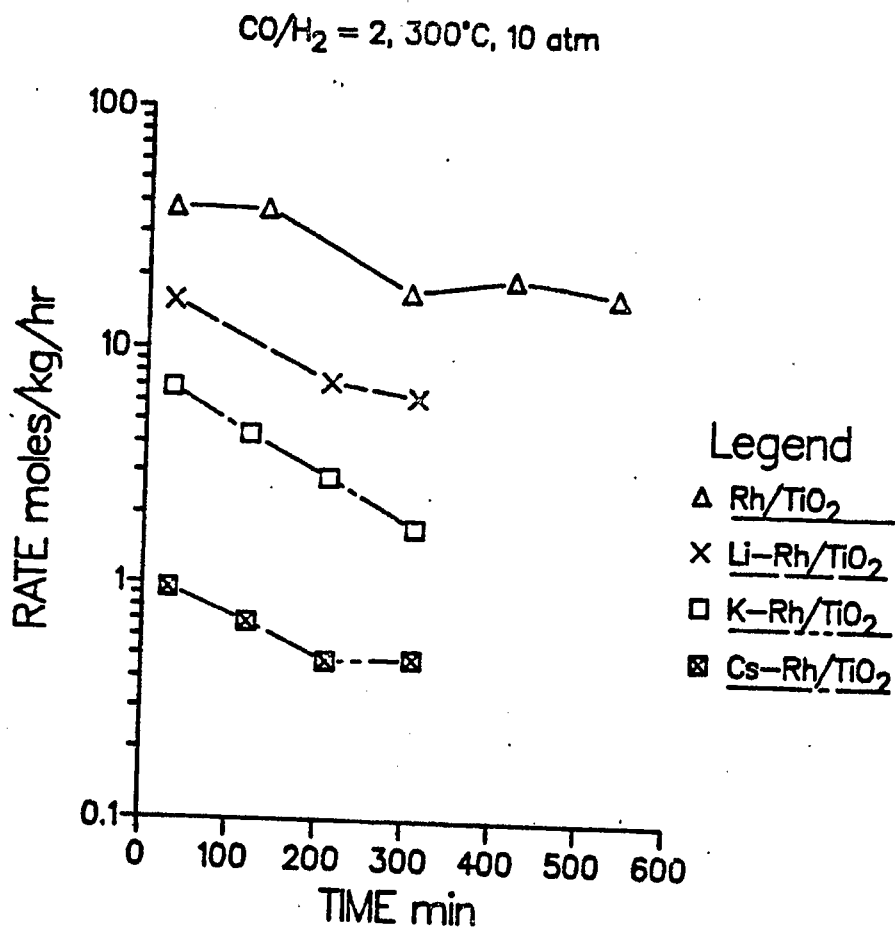


Figure 5-1 Rate of CO Conversion vs. Time over Rh/TiO₂ and Alkali-Promoted Rh/TiO₂

result of the suppression and/or slow uptake of H_2 or CO chemisorption caused by alkali promotion⁽⁴⁵⁾ and SMSI.⁽¹³⁰⁾ However, from the results of X-ray diffraction it would appear that all of the catalysts before and after reaction had average Rh particle diameters less than 4 nm. In addition, analysis of the amount of H_2 desorbed during TPD, as shown in Table 5-1, assuming all the hydrogen was adsorbed only on the metal suggests that the TiO_2 -supported catalysts had similar Rh dispersions and surface areas. However, a significant fraction of the hydrogen appears to be adsorbed on the TiO_2 .^(128,129)

The rate of CO conversion decreased in the order: unpromoted > Li > K > Cs. The unpromoted Rh/ TiO_2 exhibited a relatively stable activity after an initial decline in CO conversion during the first 300 min. The rates of formation of the major products as a function of time for Rh/ TiO_2 is shown in Figure 5-2. Since the rates of formation of all higher hydrocarbons behaved very similarly, only C_3 is shown in Figure 5-2.

Although deactivation was not exactly the same for all the catalysts, similar patterns for the rate of product formation vs. time, as shown in Figure 5-2 for Rh/ TiO_2 , were observed for both the unpromoted and the promoted catalysts. The rate of methanol formation increased with time while the rates of formation for all the other products (hydrocarbons and C_2 oxygenates) exhibited an initial decline followed by a leveling off. An increase in the rate of methanol formation with time initially has also been reported for $LaRhO_3$ ⁽³²⁾, Mn-Mo-Rh/ SiO_2 ⁽²⁹⁾, and Pd catalysts.⁽¹⁴⁴⁾

Table 5-1 Average Metal Particle Size and Chlorine Content of Rh/TiO₂ Catalysts

Catalyst	Avg. Metal Particle Diameter (Å)		Cl Content (%)
	XRD	H ₂ TPD	
TiO ₂	-	-	0.1
Rh/TiO ₂	<40	24	0.044
Li-Rh/TiO ₂	<40	27	0.43
K-Rh/TiO ₂	<40	25	-
Cs-Rh/TiO ₂	<40	36	0.39

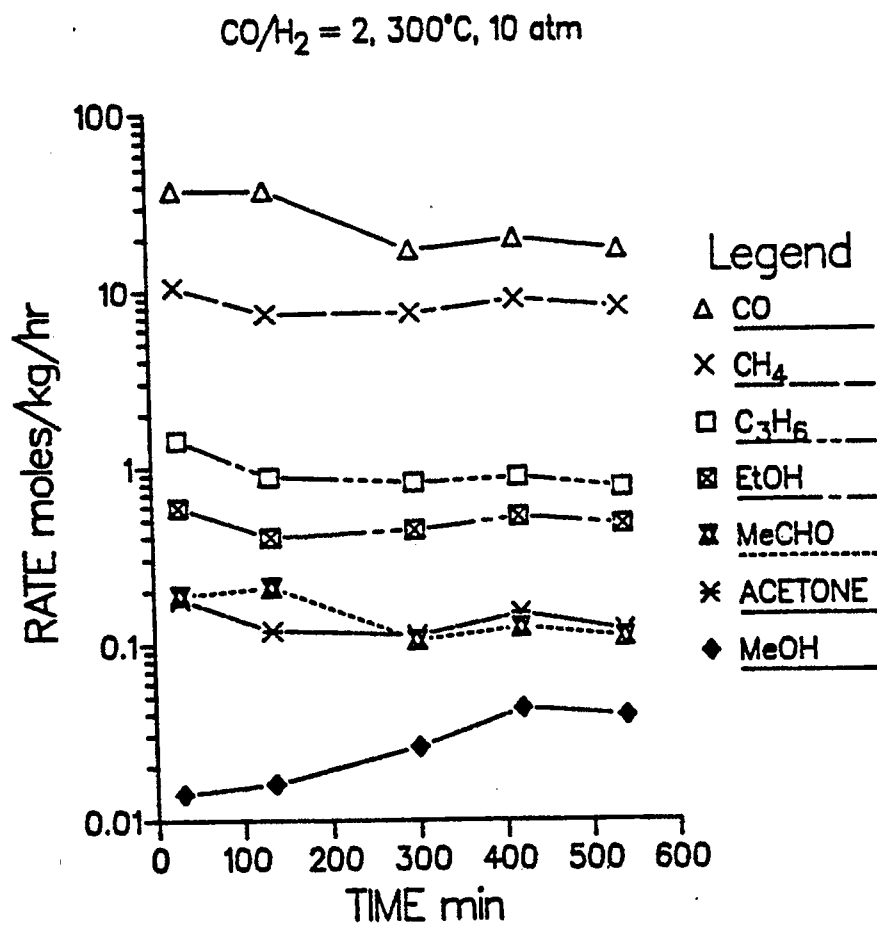


Figure 5-2 Product Formation Rate vs. Time over Rh/TiO₂

The effect of alkali promotion on the rates and selectivities of product formation is presented in Table 5-2 and 5-3. The rates for all the products formed decreased upon alkali promotion while the selectivity for oxygenated compounds increased. Similar results have also been reported for alkali-promoted Mn-Rh/SiO₂.⁽⁵⁸⁾ The Anderson-Schulz-Flory (A-S-F) distributions based on the mole fraction of both hydrocarbon and oxygenated compounds are shown in Figure 5-3 and 5-4. The oxygenated products observed were methanol, ethanol, acetaldehyde, acetone and ethyl acetate, while only trace amounts of C₃₊ straight chain oxygenated compounds were detected. Because of the lack of straight chain oxygenates above C₃ and the uncertainty in counting acetone as a C₂ or a C₃ species in A-S-F distribution, it is difficult to determine the chain growth probability for the oxygenated compounds. A detailed mechanism for the formation of acetone and ethyl acetate will be discussed later. The deviation of the C₂ mole fraction from an Anderson-Schulz-Flory distribution, as shown in Figures 5-3 and 5-4, decreased in the order: unpromoted > Li > K > Cs. The chain growth probability of hydrocarbons appeared to be affected only slightly by the alkali-promoters.

The apparent activation energies determined from Arrhenius plots for CO conversion and the formation of the major products are presented in Table 5-4. It is evident that the apparent activation energies for CO conversion and for the formation of certain products such as CH₄ and EtOH are not greatly affected by alkali promotion. This suggests that the reaction mechanism is not modified by alkali

Table 5-2 Effect of Alkali Promotion on the Product Formation Rate over Rh/TiO₂

Catalyst	Rh/TiO ₂	Li-Rh/TiO ₂	K-Rh/TiO ₂	Cs-Rh/TiO ₂
Rate of CO Conversion (moles/kg/hr)				
	17.31	6.37	1.79	0.48
Product Formation Rate (mole/kg/hr)				
CH ₄	7.56	2.70	0.67	0.10
C ₂ +	1.3	0.68	0.108	0.06
MeOH	0.026	0.024	0.008	0.0064
EtOH	0.44	0.20	0.029	0.0022
MeCHO	0.11	0.12	0.08	0.023
Acetone	0.106	0.040	0.052	0.018

Reaction Conditions: CO/H₂ = 2, 300°C, 10 atm, and 300 min time-on-stream

Table 5-3 Effect of Alkali Promotion on Product Selectivity over Rh/TiO₂

	Rh/TiO ₂	Li-Rh/TiO ₂	K-Rh/TiO ₂	Cs-Rh/TiO ₂
Selectivity (wt%) to				
CH ₄	49.9	46.6	37.7	20.6
C ₂ ⁺	32.4	31.1	15.7	33.2
Total OX*	17.7	22.3	46.5	46.1
MeOH	0.3	0.8	0.8	2.5
EtOH	8.4	9.2	4.6	1.2
MeCHO	2.0	5.4	12.4	12.8
Acetone	2.5	2.4	10.4	13.5

Reaction Conditions: CO/H₂ = 2, 300°C, 10 atm, and 300 min time-on-stream

*C₃⁺ oxygenates are included in total OX, OX: oxygenated compounds

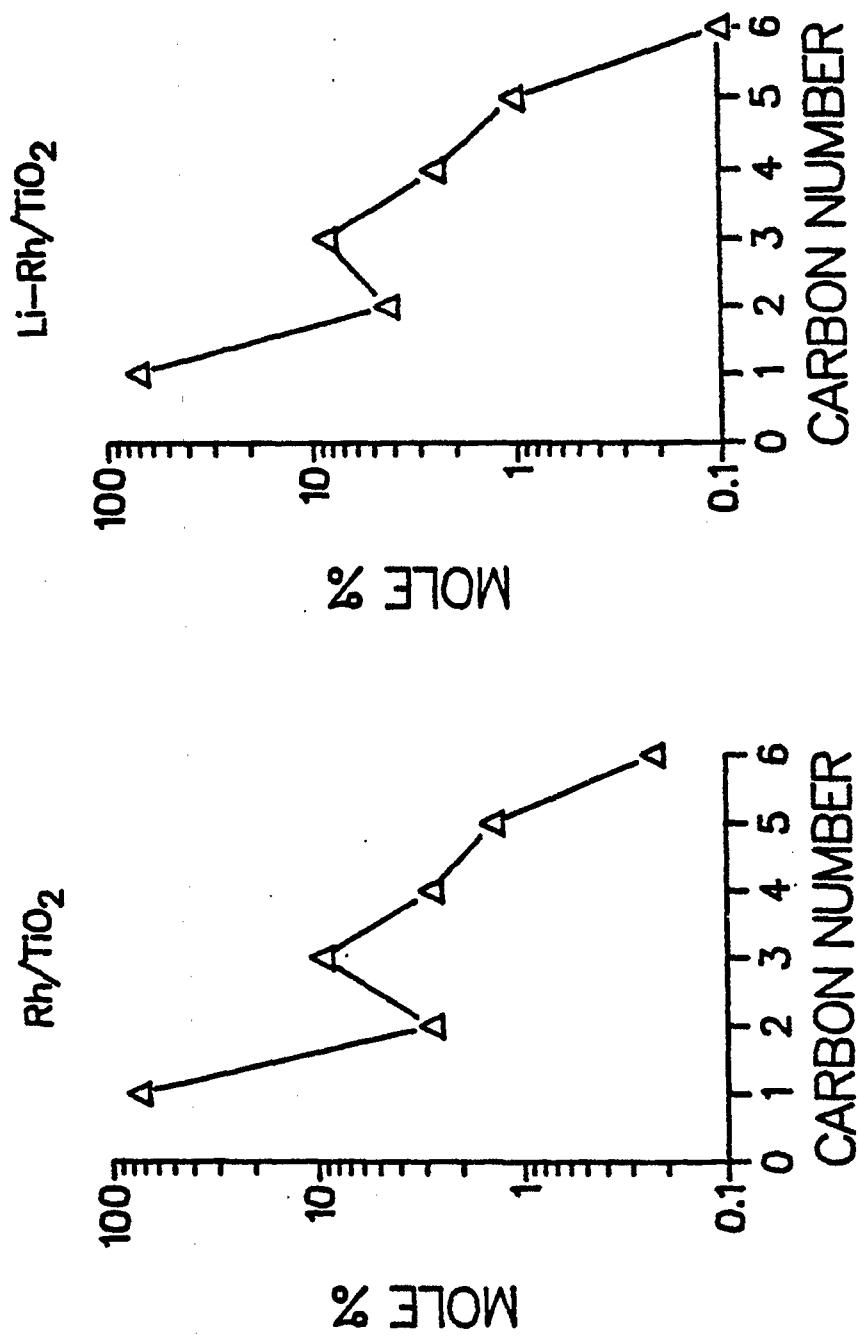


Figure 5-3 Hydrocarbon Distribution over Rh/TiO₂ and Li-Rh/TiO₂

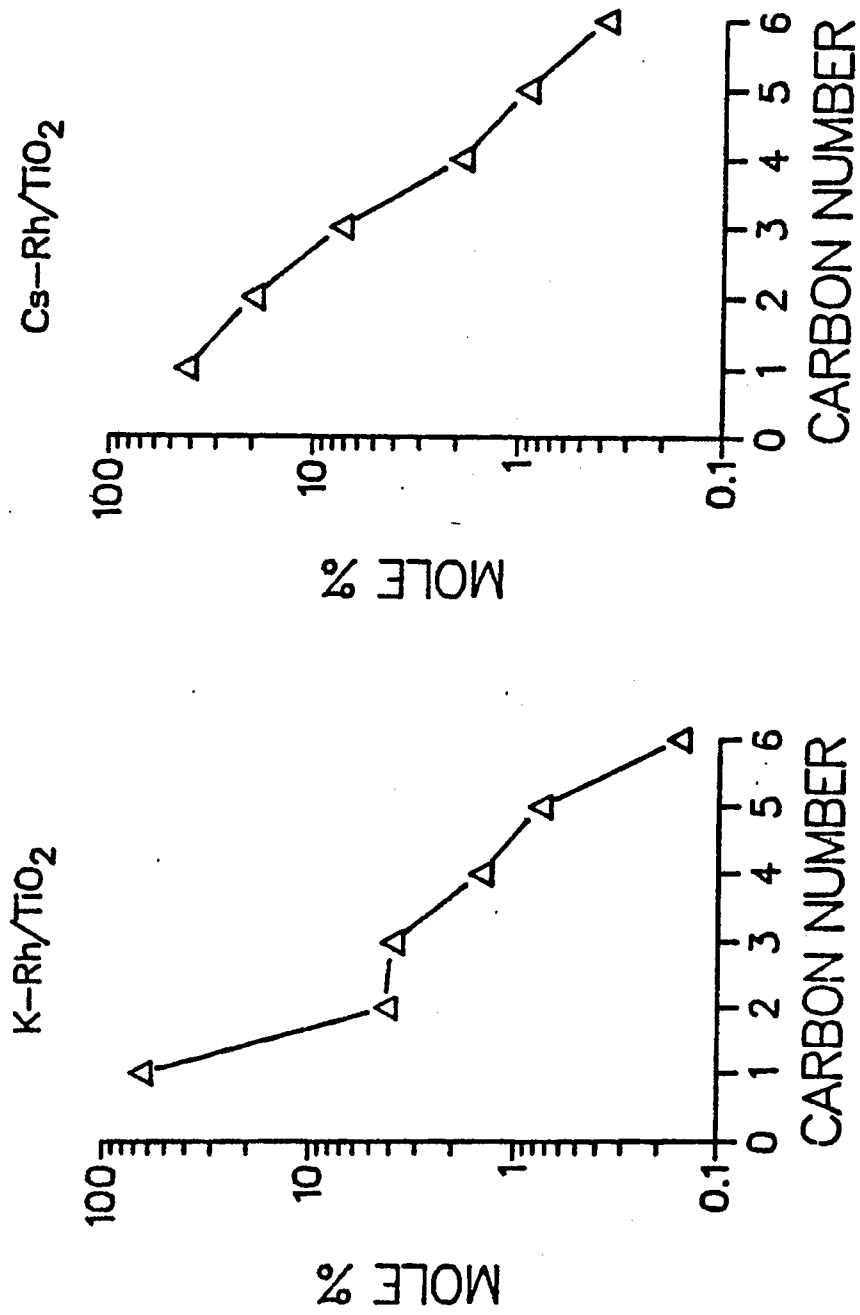


Figure 5-4 Hydrocarbon Distribution over K-Rh/TiO₂ and Cs-Rh/TiO₂

Table 5-4 Activation Energies (kcal/mole^oK) for CO Conversion and Product Formation over Rh/TiO₂ and Alkali Promoted Rh/TiO₂

	Rh/TiO ₂	Li-Rh/TiO ₂	K-Rh/TiO ₂	Cs-Rh/TiO ₂
CO Conversion	33.0	28.9	29.3	24.3
CH ₄	41.5	33.1	32.9	31.9
MeCHO	20.7	9.1	NA	23.4
EtOH	24.4	21.5	-	*
Acetone	8.7	7.4	16.9	*
MeOH	-	10.9	-	*

10 atm, CO/H₂ = 2, and 250°C 300°C
*low activity

promotion. The values for the apparent activation energy for CO conversion agrees well with those previously reported for Rh catalysts while those for CH_4 formation are somewhat high.^(32,131) The higher values for E_{CH_4} may be due to the high CO/H₂ ratio used in this study. The inconsistency of the activation energies for acetaldehyde and acetone formation among promoted and unpromoted catalysts indicates that these species may have been involved in secondary reactions.

5.2.2 Addition of Ethylene to CO/H₂

In an attempt to clarify the above findings, ethylene was added in small concentrations to the reaction mixture (2.3 mole % of the total). This addition did not result in any significant modification of the formation of products by CO hydrogenation as indicated by the constant formation rates of methane, methanol, and C₂ oxygenated compounds. The formation rates of the major products [C₂H₆, C₃+ hydrocarbons, C₂H₅CHO, and C₂H₅CH₂OH] from ethylene are shown in Table 5-5. The rate of hydrogenation of ethylene to ethane decreased by as much as 2 orders of magnitude following promotion while the total rate of formation of propionaldehyde and n-propanol decreased only by a factor of 2. It is useful to consider these two products (propionaldehyde and n-propanol) together since they are probably formed from ethylene by the same surface intermediate; a simple hydrogenation step converts the propionaldehyde to propanol. The smaller variation in the rate of propionaldehyde formation from

Table 5-5 Rates of Product Formation from Ethylene Reaction during CO Hydrogenation over Rh/TiO₂ and Alkali-Promoted Rh/TiO₂

Catalysts	rate of C ₂ H ₄ conversion (mole/kg/hr)	product formation rate (mole/kg/hr)				
		EtCHO	Propanol	CH ₄	C ₂ H ₆	Other HC's
Rh/TiO ₂	8.30	0.132	0.075	0	7.70	0.39
Rh-Li/TiO ₂	4.07	0.170	0.077	0	3.55	0.273
Rh-K/TiO ₂	1.20	0.129	0.033	0	1.02	0.011
Rh-Cs/TiO ₂	0.19	0.108	0.006	0	0.073	0.001

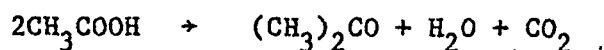
reaction conditions: CO/H₂ = 2, 300°C, 10 atm, 2.3 mole % C₂H₄

ethylene compared to that of acetaldehyde formation by CO hydrogenation is expected since propionaldehyde can be formed directly by CO insertion into the adsorbed ethylenic surface intermediate, whereas acetaldehyde is probably produced via CO insertion into a CH_x -metal species which has to be generated by CO dissociation followed by hydrogenation. (24)

5.3 Discussion

5.3.1 Formation of Acetone and Ethyl Acetate during CO Hydrogenation

The presence of acetone has been observed in the Fischer-Tropsch⁽¹⁶⁾ and higher alcohol synthesis.⁽¹⁵⁾ It has been suggested that the acetone is formed by the secondary reaction of acetic acid.⁽¹⁶⁾



However, acetic acid was not observed in this study during steady state reaction conditions over Rh/TiO_2 and alkali-promoted Rh/TiO_2 . In addition to the above reaction, Schulz and Zein El Deen⁽¹⁸⁾ have proposed that acetone may be formed from a combination of the acetaldehyde surface intermediate and a surface methyl species. The fact that the selectivity of acetone parallels that of acetaldehyde, as shown in Table 5-3, supports such a conclusion. In contrast to our results, acetone was not observed during CO hydrogenation over Rh/TiO_2

by Katzer et al.⁽⁶⁾ or by Ichikawa.⁽¹²⁾ The failure of these authors to observe acetone may have been due to low reaction temperatures, low CO/H₂ ratios, different catalyst preparation methods, and/or different reduction conditions. Dry⁽¹⁶⁾ has pointed out that acetone is always present during F-T synthesis at high reaction temperatures.

It is obvious that ethyl acetate could have been formed by the esterification of ethanol with acetic acid. However, there exist other possible routes for forming ethyl acetate not requiring acetic acid. Recently, Morrison et al.⁽¹³²⁾ have shown that a ketene complex is able to react with methanol to form methyl acetate. A ketene surface species has also been suggested to be a surface intermediate for forming C₂ oxygenated compounds, as discussed in the previous section. Thus, the ethyl acetate may have been formed from a reaction of ketene intermediates with adsorbed ethanol. Although there are alternative pathways to form acetone and ethyl acetate not requiring the presence of acetic acid, the reaction pathways to these two species via acetic acid still can not be ruled out. At high reaction temperatures, acetic acid could easily be depleted by secondary reactions and esterification.

5.3.2 Effect of Alkali Promotion

The effects in general of alkali promotion on CO hydrogenation over group VIII transition metal catalysts have been identified by numerous researchers⁽⁴⁴⁻⁴⁷⁾ as (a) a suppression of hydrogenation ability, (b) an increase in the ability to dissociate CO, (c) an

increase in the selectivity to long chain hydrocarbons, and (d) a decrease in CO conversion activity. It would be expected that similar effects of alkali promotion might occur for Rh catalysts. The suppression of hydrogenation was evidenced by an increase in the ratios of C₃-C₅ olefins-to-paraffins and of acetaldehyde-to-ethanol upon alkali promotion, as presented in Table 5-6.

The "supposed" electron donation properties of the alkali promoters⁽⁵⁸⁾ should decrease the average surface oxidation state. This should result in a decrease in the product selectivity toward oxygenated compounds if Rh in the oxide state is responsible for oxygenate formation. On the contrary, upon alkali promotion, product selectivity for oxygenated compounds increased while the formation rates for all the products decreased (Tables 5-2 and 5-3). This clearly indicates that there was less suppression in the rate of oxygenated product formation than in that of hydrocarbon formation. Results of ethylene addition also indicate that the CO insertion step to form oxygenated compounds over Rh/TiO₂ is not strongly affected by the chemical nature of the alkali-promoter. If the enhancement of CO dissociation did occur on the alkali-promoted Rh catalysts, it seemed to have little effect on CO insertion. The decrease in the rate of formation of oxygenated compounds upon alkali promotion may have been mainly due to a lower rate of formation of the precursor, CH_x, as result of hydrogenation suppression by alkali-promoters since CO insertion was not strongly affected. The smaller deviation in mole fraction of ethylene upon alkali promotion as shown in Figures 5-3 and

Table 5-6 Effect of Alkali Promotion on the [MeCHO]/[EtOH]
and Olefin Selectivities over Rh/TiO₂

	Rh/TiO ₂	Li-Rh/TiO ₂	K-Rh/TiO ₂	Cs-Rh/TiO ₂
[MeCHO]/[EtOH]	0.25	0.61	2.79	10.45
[C ₃ ^α -C ₅ ^α]/[C ₃ -C ₅]	2.7	5.8	4.6	4.2

Reaction Conditions: 300°C, 10 atm, 300 min time-on-stream

*before ethylene addition

5-4 may be due to the lower rate of incorporation of ethylene into higher hydrocarbons on alkali-promoted catalysts. The ethylene addition study showed that the rate of incorporation of ethylene into higher hydrocarbons decreased in the order: unpromoted > Li > K > Cs.

The effect of alkali promotion to decrease overall activity of Rh catalysts for CO hydrogenation at temperatures above 275°C and pressures above 10 atm has been reported by van den Berg⁽²⁹⁾, Wilson et al.⁽¹³¹⁾, and this study. Contradictory results reported by Orita et al.⁽¹³⁾ and Kagami et al.⁽¹⁴⁾ for alkali-promoted Rh/TiO₂ and Rh/Al₂O₃ have shown the alkali promoter increases the formation rate of oxygenated compounds under low temperature and low pressure conditions (180°C and < 1 atm). They have suggested that the active sites may be located near the juncture of the rhodium metal and the support and that those sites are modified by the addition of alkali ions. The difference in reaction conditions may be related to these contradictions. It has been suggested that Rh catalysts can dissociate adsorbed CO at temperatures of 200-300°C.⁽²¹⁾ Thus, alkali promotion may enhance CO dissociation excessively at high temperatures (>200°C) resulting in a high coverage of carbon species and leading to a decrease in overall activity. However, such a promotion of CO dissociation at low temperatures (<200°C) may greatly increase the formation rate of CH_x, a precursor for CO insertion, without contributing to catalyst deactivation.

5.4 Conclusions

The selectivity and activity of CO hydrogenation over Rh catalysts vary with the presence of alkali promoters. The effect of alkali promotion on Rh/TiO₂ can be summarized as follows:

- a. Alkali promoters have a different effect on the formation of oxygenated compounds than on that of hydrocarbons.
- b. The selectivity for oxygenated compounds increase in the order: unpromoted < Li < K = Cs.
- c. The abilities for hydrogenation in general and ethylene incorporation to higher hydrocarbons decrease in the order: unpromoted > Li > K > Cs.
- d. The ability for CO insertion is only a relatively weak function of promotion. This fact combined with the decrease in hydrogenation activity probably accounts for the increase in oxygenated selectivity upon promotion.
- e. The chain growth probability is only slightly modified by the presence of alkali promoters.

6.0 EFFECT OF ALKALI PROMOTION OF Rh/La₂O₃

6.1 Background

Among supported Rh catalysts, Rh/La₂O₃ is known to be highly selective for the synthesis of oxygenates from synthesis gas.⁽⁶⁾ A study of alkali promotion of Rh/La₂O₃ would help to elucidate the interaction among promoter, support, and Rh metal and the limitations of alkali promotion in modifying oxygenate selectivity. Small amounts of olefins (ethylene and propylene) and ethanol were added to the H₂/CO reactant mixture under synthesis conditions in an attempt to determine the effect of alkali promotion on specific reaction steps such as CO insertion, hydrogenation, and secondary reaction of primary products. The relationship between the synthesis of C₂ oxygenates from CO and H₂ and the synthesis of C₃ oxygenates from CO/H₂/C₂H₄ was investigated.

6.2. RESULTS

The average metal particle sizes of Rh/La₂O₃ and alkali-promoted Rh/La₂O₃ are presented in Table 6-1. The variation of rate of product formation with time is shown in Figure 6-1. The activity is expressed in mole/kg/hr because of the uncertainty in the estimation of the number of active surface atoms in alkali promoted catalysts. The rate of CO conversion and the rate of formation for all the products except MeCHO showed a slight initial decline and then remained essentially

Table 6-1 The Average Metal Particle Sizes of Rh/La₂O₃
and Alkali-Promoted Rh/La₂O₃

Catalysts	Average Particle Diameter Å
Rh/La ₂ O ₃	27.5 (a) < 30 (b)
Li-Rh/La ₂ O ₃	< 30 (b)
K-Rh/La ₂ O ₃	< 30 (b)
Cs-Rh/La ₂ O ₃	< 30 (b)

(a) Determined by hydrogen TPD in flowing Ar at atm
(b) X-ray diffraction

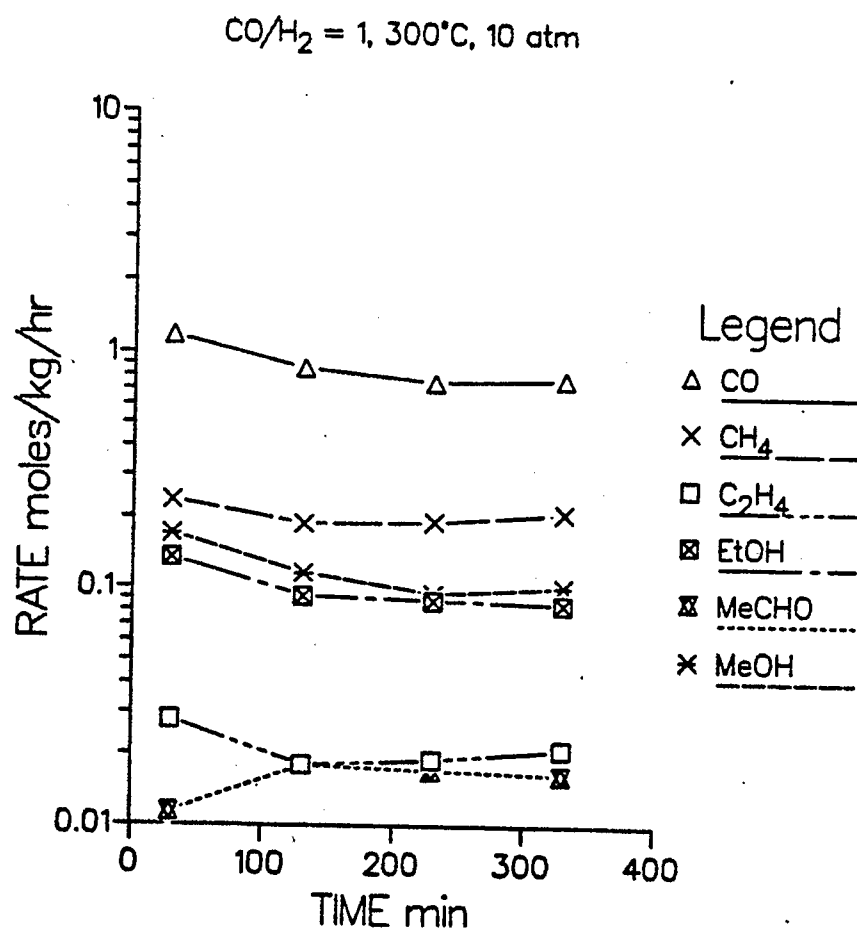


Figure 6-1 Product Formation Rate vs. Time over $\text{Rh}/\text{La}_2\text{O}_3$

constant for at least 24 hours. A variation in the ratio of MeCHO/EtOH was observed only in the first two hours.

The effect of temperature on the product distribution is shown in Table 6-2. Methanol was the major product for temperatures at or below 255°C. The selectivity for C₂ oxygenated compounds exhibited a maximum for a reaction temperature of approximately 286°C. Similar trends in product selectivity have also been observed for LaRhO₃ for reaction conditions of 225-375°C and 6 atm⁽³²⁾, but the maximum selectivity for C₂ oxygenates in that case occurred near 300°C.

6.2.1 Effect of Alkali Promotion

Reaction temperature evidently can have great effects on product distributions over Rh catalysts. It is therefore useful to compare the product selectivity for alkali-promoted and unpromoted catalysts at several different reaction temperatures. As shown in Figure 6-2, the C₂ oxygenate selectivity appears to be somewhat more sensitive to alkali promoters at higher temperatures than at lower temperatures. Since the variation in methanol and C₂ oxygenate selectivities among promoted and unpromoted catalysts showed similar trends at different temperatures, it may be expected that the apparent activation energies for the formation of these products are not greatly changed by alkali promotion in the temperature range of 255-300°C. The apparent activation energies determined from Arrhenius plots for the formation of the major products are presented in Table 6-3. It is evident that the apparent activation energy for methane formation is essentially

Table 6-2 The Effect of Temperature on the Product Distribution from CO Hydrogenation Over Rh/La₂O₃

Reaction Temperature (°C)	255	270	286	300
Activity (Mole/Kg Hr)	0.212	0.322	0.548	0.772
Selectivity (Wt %)				
C ₁	6.9	11.2	16.2	22.8
C ₂ ⁺	10.7	12.4	15.5	18.9
MeOH	56.7	43.2	28.7	21.6
EtOH	17.0	22.5	28.7	26.0
MeCHO	5.4	5.2	4.8	4.8
Total OX	82.4	76.4	68.3	58.3

CO/H₂ = 1, GHSV:1100 hr⁻¹, 10 atm
 Acetone, EtAc, and C₃-C₄ OX are included in Total OX

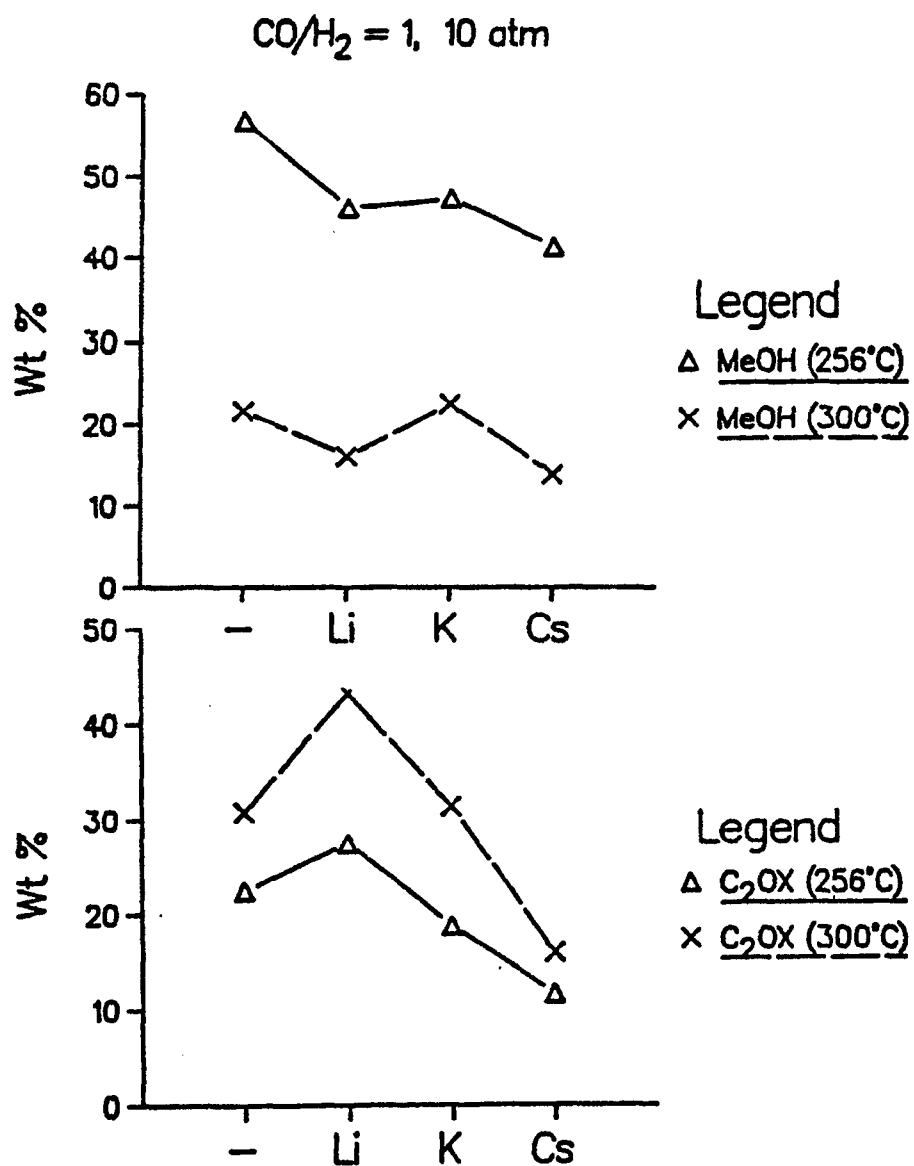


Figure 6-2 The Oxygenate Selectivities over Alkali-Promoted and Unpromoted Rh/La₂O₃ at 256 C and 300 C

Table 6-3 Activation Energies for the Formation of Major Product over Rh/La₂O₃ and Alkali Rh/La₂O₃

	Rh/La ₂ O ₃ (a)	Li-Rh/La ₂ O ₃ (a)	K-Rh/La ₂ O ₃ (a)	Cs-Rh/La ₂ O ₃ (a)	Rh/La ₂ O ₃ (b)	LaRhO ₃ (c)	Rh ₂ O ₃ (d)	Rh/La ₂ O ₃ (e)
CH ₄	32.5	35.5	31.7	34.2	28	27±2	26	33.4
C ₂ H ₄	29.6	31.0	31.4	-	-	27±2	26±2	33.4
MeCHO	13.9	20.5	24.9	23.1	-	28±2	26±2	-
EtOH	23.9	33.2	26.7	31.0	20	26±2	-	28.2
Acetone	21.7	29.5	23.9	30.0	-	-	-	-
1-Propanol	33.4	31.7	31.0	-	-	-	-	-
MeOH	-	9.4	7.2	-	12	16±3	16±4	19.1

- (a) This work, 10 atm, 250-300°C.
 (b) Ichikawa (32) CO/H₂ = 1, 0.1 atm, 180-250°C.
 (c) Watson and Somorjai (32) CO/H₂ = 1, 6 atm, 220°C-380°C.
 (d) Matyjas and Somorjai, (124) CO/H₂ = 1, 6 atm, 250-330°C.
 (e) Via (110), CO/H₂ = 1/3, 40 atm, 227-277°C.

not affected by alkali promotion. Its values are, however, somewhat higher than those previously found for Rh-containing catalysts in studies at 0.1 atm⁽¹²⁾ and 6 atm^(32,124) and range very close to those found under reaction conditions of 40 atm and 227-277°C.⁽¹¹⁰⁾ Although the apparent activation energies for other major products showed a slight variation from unpromoted to promoted catalysts, all the values except those for CH₃OH and MeCHO fell into the range of literature data, as shown in Table 6-3. Since the activation energy for product formation decreases in the order: CH₄ > C₂OX > CH₃OH, it is possible to obtain a high selectivity in methane and methanol by varying the reaction temperature. Since the trends in product selectivities among promoted and unpromoted catalysts are similar at different temperatures, it is convenient to compare the performance of these catalysts at 300°C and 10 atm.

As shown in Table 6-4, Li-promoted catalysts exhibited an increase in the rate of CO conversion and the selectivity for C₂ oxygenates and a decrease in methane selectivity. Unless otherwise stated, reaction results for the promoted catalysts will always be compared to those for the unpromoted catalyst. The rate of CO conversion and the rates of formation for all the products decreased for the K-promoted catalyst while product selectivities were only slightly affected. The Cs-promoted catalyst exhibited decreases not only in the rates of formation of all the products but also in the selectivity toward the oxygenated compounds. The Anderson-Schulz-Flory (A-S-F) distributions based on the mole fractions both of

Table 6-4 Effect of Alkali Promotion on the Product Selectivity over Rh/La₂O₃

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
Rate of CO Conv. to OX and HC (mole/kg/hr)	0.772	1.02	0.348	0.213
<u>Selectivity wt. %</u>				
CH ₄	22.8	10.0	14.1	24.5
C ₂ +	18.9	22.1	21.3	32.7
Total OX*	58.3	67.9	64.6	42.8
MeOH	21.6	16.0	22.5	13.8
C ₂ OX	31.5	43.1	31.4	15.8
Activity (mole/kg/hr)				
CH ₄	0.114	0.126	0.059	0.057
C ₂ +	0.07	0.110	0.038	0.03
MeOH	0.102	0.101	0.048	0.016
C ₂ OX	0.100	0.190	0.047	0.013

Reaction Conditions: 300°K, 10 atm, CO/H₂ = 1 and CHSV: 1,100 hr⁻¹
 *Acetone, EtAc, and C₃ - C₄ OX are included in Total OX.

hydrocarbons and oxygenated compounds are shown in Figure 6-3 and 6-4. Because of the lack of straight chain oxygenates above C_3 , it is difficult to determine chain growth probabilities for the oxygenated compounds. Although alkali promoters have little effect on the chain growth probability of hydrocarbons, they do affect the mole fraction of C_2 hydrocarbons. The deviation of the mole fraction of C_2 hydrocarbon from the linear A-S-F distribution decreases in the order: unpromoted, $Cs > Li > K$. These results are somewhat different from those reported for alkali-promoted Rh/TiO_2 in Chapter 5.

6.2.2 Addition of Ethylene to CO/H_2

A small amount of ethylene (2.6 mole %) was added to the CO/H_2 reaction mixture to clarify the effect of alkali promotion on specific reactions occurring during synthesis. As shown in Figure 6-5, ethylene was added to CO/H_2 reactant mixture after 800 minutes of reaction and then was continued for 120 minutes. Although the formation rates of certain products at 1160 min. (180 min after the ethylene addition was stopped) were still somewhat higher than those before ethylene addition (Figure 6-5), the rates of formation for all the products essentially returned to values existing prior to ethylene addition. A similar procedure was also used for propylene and ethanol addition.

The rates of formation of acetaldehyde (as seen in Figure 6-5), methane, methanol, ethanol and acetone (not shown in Figure 6-5) were virtually unaffected during ethylene addition. This indicates that CO

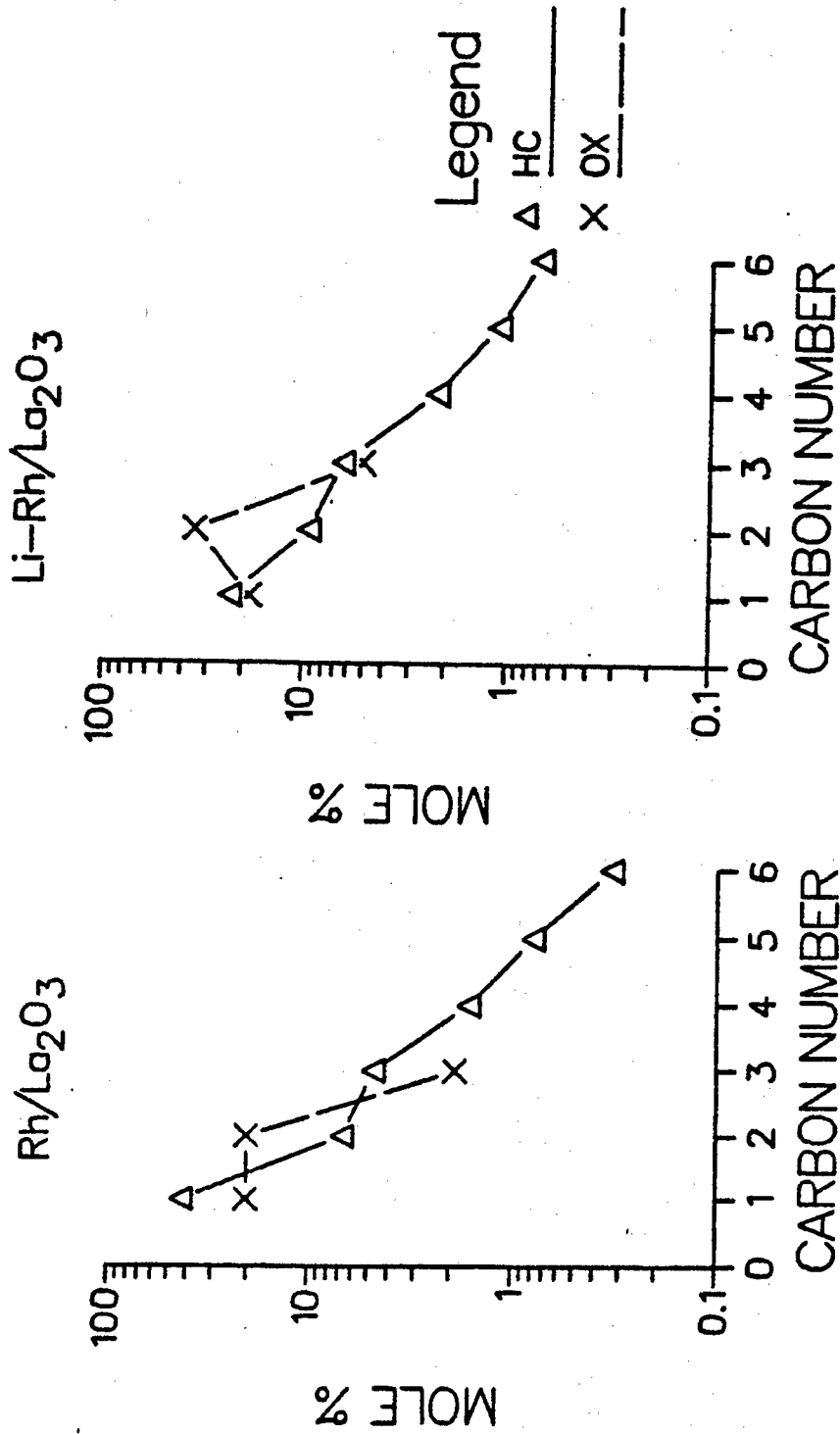


Figure 6-3 Product Distribution over Rh/La₂O₃ and Cs-Rh/La₂O₃

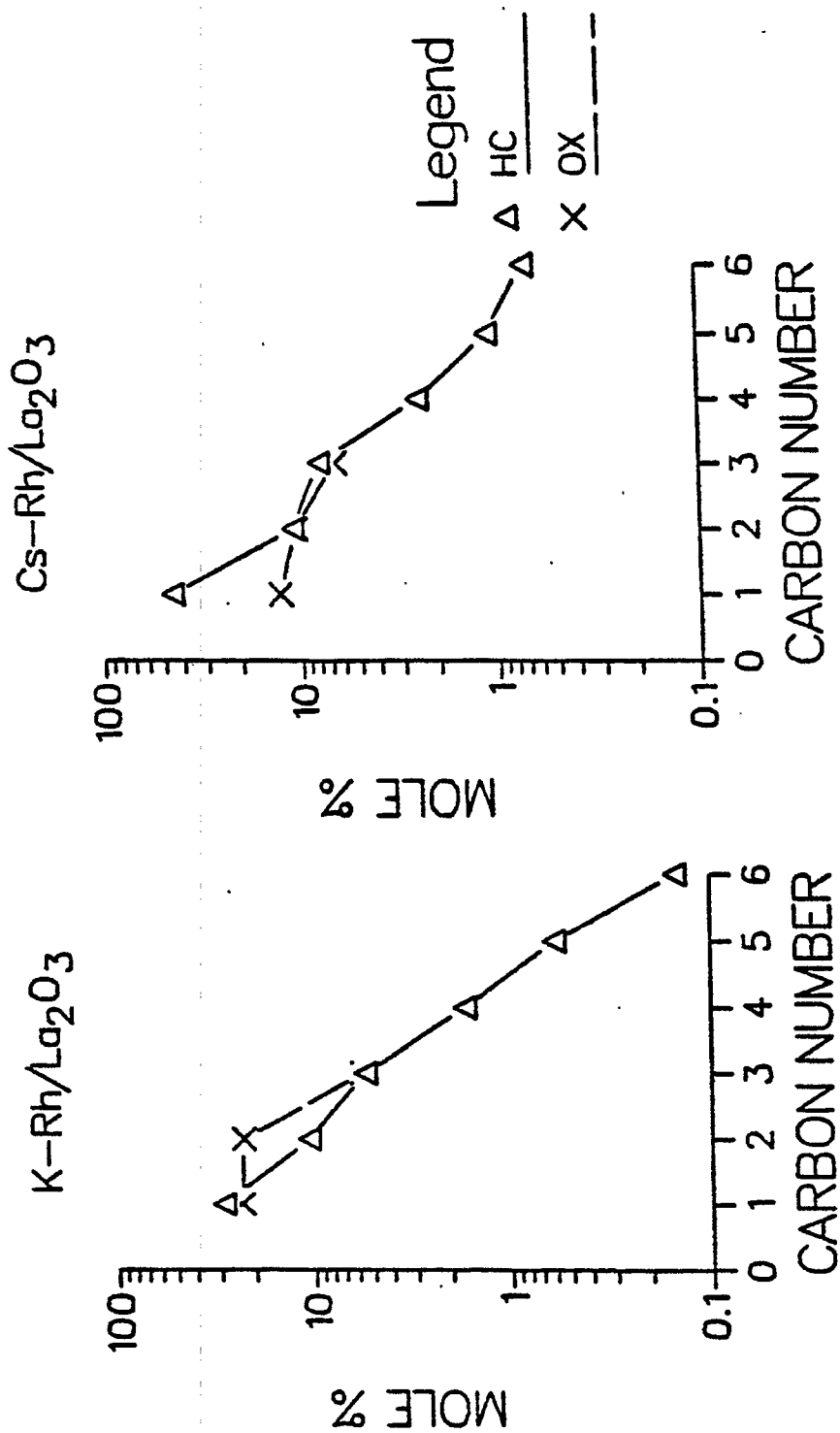


Figure 6-4 Product Distribution over K- Rh/La₂O₃ and Cs-Rh/La₂O₃

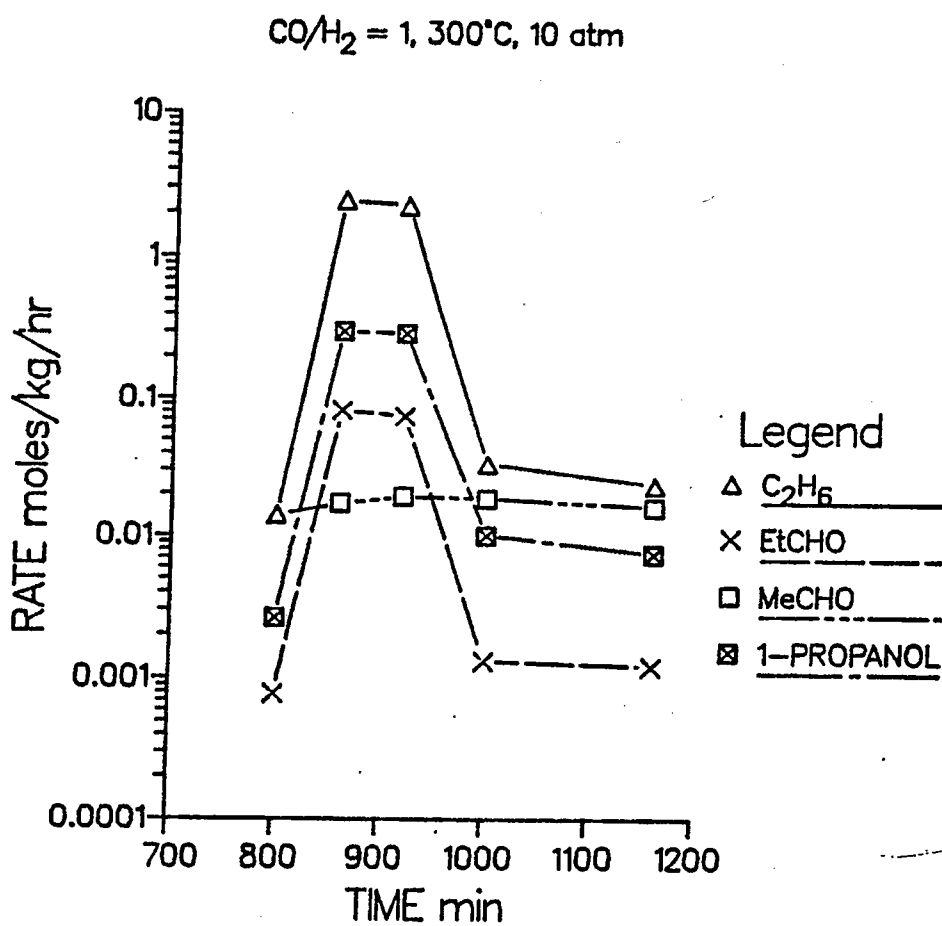


Figure 6-5 Rate of Product Formation during Addition of Ethylene to CO/H_2

hydrogenation to methane, methanol, C_2 oxygenated compounds, and acetone were not influenced by the added ethylene. The increase in the formation rate of some products, such as ethane, 1-propanol and propionaldehyde, can be assumed to result primarily from the added ethylene. By determining the differences in the rates of product formation during and after the addition of ethylene, the rates of hydrogenation, chain incorporation, and hydrocarbonylation of ethylene could be estimated (Table 6-5). As indicated by the constant rate of formation of methane on promoted and unpromoted catalysts before, during, and after ethylene addition, it appears that hydrogenolysis of ethylene did not occur to any noticeable extent. Li-promotion promoted the rate of formation of C_3 oxygenated compounds while a marked decrease was observed for the Cs-promoted catalyst. K-Rh/La₂O₃ also exhibited lower rates of formation relative to Rh/La₂O₃ of both C_3 oxygenated compounds and C₂H₆ (by a factor of approximately 2). The low activities for the incorporation of ethylene into C₃₊ hydrocarbons is expected since Rh metal is known to be a poor catalyst for catalyzing the incorporation of ethylene into higher hydrocarbons.⁽⁷³⁾ K and Cs promoters, however, appear to promote this incorporation of ethylene into C₃₊ hydrocarbons on Rh/La₂O₃.

6.2.3 Addition of Propylene to CO/H₂

The results of propylene addition are presented in Table 6-6. The rate of propylene hydrogenation decreased by a factor of 10 for the Cs-promoted catalysts. The ratio of n-butyraldehyde/iso-

Table 6-5 Product Selectivity from Ethylene Reaction during CO hydrogenation over Rh/La₂O₃ and Alkali-Promoted Rh/La₂O₃

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
Rate of C ₂ H ₄ Conversion mole/kg/hr	2.528 (32%) (a)	2.639 (33%)	1.231 (16%)	0.209 (2.7%)
Rate of Product Formation mole/kg/hr				
C ₂ H ₆	2.170(85.8) (b)	2.210(83.7)	1.020(82.8)	0.119(56.9)
C ₃ +	0.008(0.3)	0.009(0.3)	0.069(5.6)	0.035(16.7)
EtCHO	0.072(2.8)	0.127(4.8)	0.049(4.0)	0.041(19.6)
1-Propanol	0.278(11.1)	0.293(11.1)	0.093(7.6)	0.014(6.7)

2.6 mole % of C₂H₄ in CO/H₂ = 1, at 300°C and 10 atm.

(a) % conversion of ethylene
(b) product selectivity (mole %)

Table 6-6 Product Selectivity from Propylene Reaction during CO Hydrogenation over Rh/La₂O₃ and Alkali-Promoted Rh/La₂O₃

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃
Rate of C ₃ H ₆ Conversion (mole/kg/hr)	0.294 (a) (3.2%) (b)	0.147 (1.6%)	0.158 (1.7%)	0.0263 (0.3%)
Rate of Product Formation (mole/kg/hr)				
C ₃ H ₆	0.243 (82.6) (b)	0.106 (72.1)	0.14 (88.6)	0.019 (72.2)
C ₄ +	0.046 (15.6)	0.037 (25.1)	0.014 (8.8)	0.0063 (23.9)
Iso C ₃ H ₇ CHO	0.0013 (0.4)	0.001 (0.7)	0.0013 (0.8)	0.00052 (2.0)
N-C ₃ H ₇ CHO	0.0037 (1.3)	0.0028 (2.0)	0.0028 (1.8)	0.00049 (1.9)

3 mole% of C₃H₆ in CO/H₂ = 1 at 300°C and 10 atm

(a) (% conversion of propylene)

(b) product selectivity mole %

butyraldehyde and the formation rate of n-butyraldehyde and isobutyraldehyde were only slightly affected by Li and K promotion but were greatly decreased for the Cs promotion case. In comparison to ethylene, propylene showed a much lower activity toward both hydrogenation and hydrocarbonylation and a lower selectivity toward oxygenated compounds.

6.2.4 Addition of Ethanol to CO/H₂

The amount of ethanol added was controlled in the range of 0.1-0.99 mole % of the CO/H₂ reactant mixture. The only possible effect of the concentration of added alcohols on the reaction of alcohols is the selectivity toward the formation of ether.⁽¹³⁴⁾ However, ether is known to decompose readily on Rh metal at temperatures above 200°C.^(79,100) Thus, it is not surprising that ether was not formed in this case at 300°C. Although the amounts of ethanol added were not equal for each catalyst, the trend of relative rates and selectivities of specific reactions such as dehydration, dehydrogenation, conversion of ethanol to methane and chain incorporation still can be clearly discerned. As shown in Table 6-7, the selectivity for decomposition of ethanol to CH₄ and dehydration of ethanol to C₂ hydrocarbons decreased in the order: unpromoted > Li > K, Cs. The selectivity for dehydrogenation of ethanol increased in the order: unpromoted < Li < K, Cs, although overall activity was very low for both K- and Cs-Rh/La₂O₃. Besides the reaction of ethanol, the addition of ethanol resulted in a decrease in rates of formation of methanol and C₃

Table 6-7 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Rh/La₂O₃ and Alkali-Promoted Rh/La₂O₃

	Rh/La ₂ O ₃	Li-Rh/La ₂ O ₃	K-Rh/La ₂ O ₃	Cs-Rh/La ₂ O ₃	La ₂ O ₃
X EtOH Added	0.11	0.28	0.47	0.68	0.99
Overall Rate, mole/kg/hr (X conv.)	0.27 (81%)	0.15 (18%)	0.038 (2.7%)	0.002 (0.09%)	0.028 (1%)
Selectivity (mole %)					
CH ₄	84.0	58.0	0	0	0
C ₂	6.0	19.4	0	0	0
C ₃ +	9.0	3.6	0	0	0
MeCHO	0.5	19.0	100	100	100
Acetone	0.5	0	0	0	0
Decrease in Product Formation Rate During EtOH Addition mole/kg/hr					
MeOH	0.04	0.03	0.01	0.007	-
C ₃ O _X	0.007	0.017	0.004	0	-

300°C, 10 atm, and CO/H₂ = 1

oxygenates for both promoted and unpromoted catalysts. Addition of ethanol to CO/H₂ was also carried out over La₂O₃ to determine the contribution of La₂O₃ to the decomposition of ethanol. La₂O₃, as seen in Table 6-7, did not exhibit any dehydration or conversion of ethanol to methane activity but it did exhibit dehydrogenation activity at these reaction conditions (300°C and 10 atm).

6.3 Discussion

6.3.1 Effect of the Addition of Ethylene, Propylene, and Ethanol to CO/H₂ on Product Distribution

The addition of ethylene to CO/H₂ resulted in a significant increase in rates of formation of C₃ oxygenates and ethane indicating that ethylene (Table 6-5) is very active in reactions with CO and H₂ under synthesis conditions. The fact that the rates of formation for methane, methanol, ethanol, acetaldehyde, acetone, and ethyl acetate did not change significantly before, during and after the addition of ethylene for alkali promoted and unpromoted catalysts indicates that the reaction pathways to these compounds were not affected by the added ethylene. This also suggests that hydrogenation and hydrocarbonylation of ethylene do not compete with CO hydrogenation (formation of CH_x, C_yH_x, MeOH, C₂O_x, etc., from CO and H₂) for adsorbed CO and H and for active sites. The constant rate of formation of methane before, during, and after the addition of ethylene also suggests that hydrogenolysis of ethylene did not occur to any extent.

Figure 6-6 shows a comparison of the rate of C_2 oxygenate formation from CO hydrogenation with the rate of C_3 oxygenate formation from the reaction of ethylene with CO/H₂ for promoted and unpromoted Rh/La₂O₃. The rate of C_2 oxygenate formation parallels those of C_3 oxygenate formation. This suggests that a catalyst which is active in catalyzing the formation of acetaldehyde and ethanol during CO hydrogenation is also active in catalyzing the formation of propionaldehyde and propanol during reaction of ethylene with CO/H₂. In other words, a catalyst which is active in catalyzing CO insertion into adsorbed CH_x is also active in catalyzing CO insertion into the adsorbed C₂H_x. However, the trend in the effect of alkali promotion on CO insertion into adsorbed C₃H_x is not as obvious as for CO insertion into the adsorbed C₂H_x (Table 6-5 and 6-6).

From Tables 6-5 and 6-6, it can be seen that the rate of CO insertion into an adsorbed C₃ alkyl group is much slower than that of CO insertion into an adsorbed C₂ alkyl group. A similar trend has also been observed in hydroformylation over zeolite-supported Rh.⁽¹³³⁾ It has been suggested that the activity of CO insertion into alkyl groups over Rh decreases in the order: CH_x > C₂H_x > C₃H_x.⁽²⁹⁾ If this is the case, the lower formation rate of C₂ oxygenates during CO hydrogenation compared with that of C₃ oxygenates during the reaction of ethylene with CO/H₂ may be attributed to a slow formation rate of CH_x for CO insertion. It has been proposed that the rate determining step for the formation of C₂ oxygenates is the formation of CH_x.⁽³²⁾

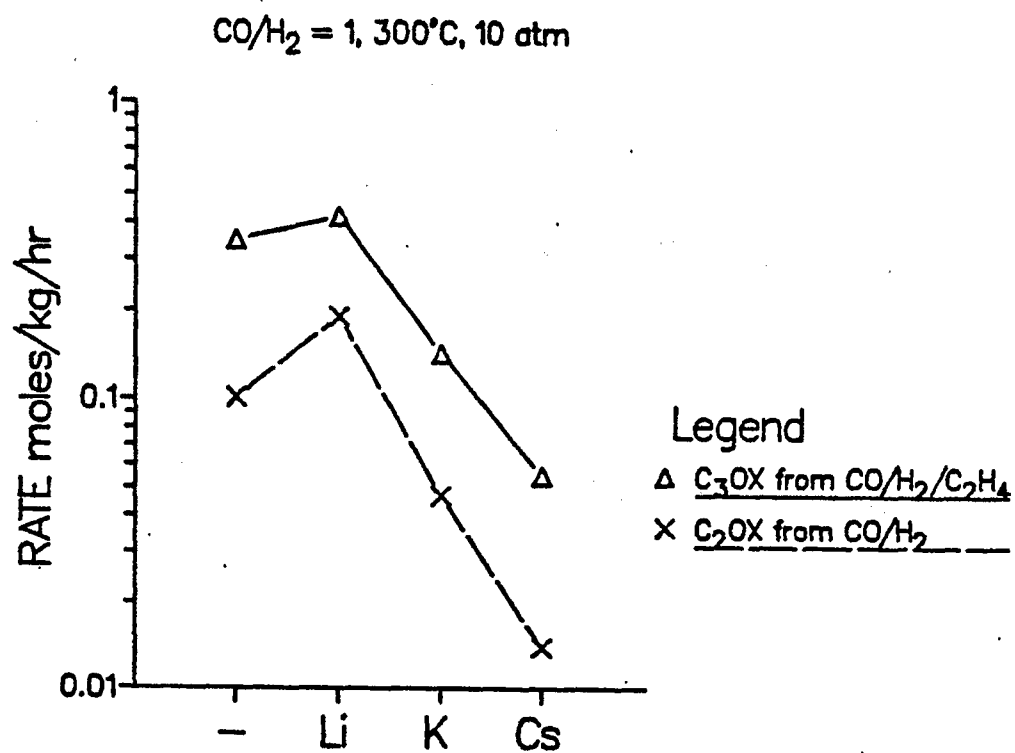


Figure 6-6 A Comparison of the Rate of C_2 Oxygenate Formation during CO Hydrogenation with that of C_3 Oxygenate Formation during Addition of Ethylene to CO/H_2

The insertion of CO into alkyl groups is well known to occur on Rh complexes.^(135,136) In this study, it is still not clear whether the formation of C₃ and C₄ oxygenates during ethylene and propylene addition occurred homogeneously on some Rh complexes. Although the formation of Rh complexes is not favored at 300°C, 10 atm, and CO/H₂ = 1.⁽²⁹⁾ Takahashi and Kobayashi⁽¹³³⁾ have observed that Rh/SiO₂ and Rh/Al₂O₃ are active for hydroformylation of ethylene for a long period of time without deactivating at 127°C and 1 atm. This suggests that hydroformylation may be carried out on the Rh surface without loss of the active metal via the gas phase. Takahashi et al.⁽¹³⁶⁾ have proposed a surface hydroformylation mechanism to explain their kinetic results obtained from zeolite-supported Rh catalysts. Ichikawa et al.⁽¹¹⁵⁾ and Orita et al.⁽¹²⁷⁾ have demonstrated by isotopic labelling studies that C₂ oxygenates are formed via CO insertion into surface CH₂/CH₃ species. Castener et al.⁽¹²⁴⁾ have also shown that the surface of Rh₂O₃ is active in catalyzing CO insertion into adsorbed alkyl groups. All of this evidence strongly supports the case for formation of C₂₊ oxygenates on the surface of Rh catalysts.

As can be seen in Table 6-7, the addition of ethanol to CO/H₂ resulted in a decrease in the formation rates of methanol and 1-propanol without decreasing the formation rates of hydrocarbons. This indicates that (a) the added ethanol may strongly adsorb on the active sites for the formation of oxygenates, inhibiting the formation of methanol and 1-propanol and (b) the active sites for the formation of oxygenates are different from those for the formation of

hydrocarbons. A dual site mechanism has been proposed previously to explain the formation of hydrocarbons and oxygenates over Rh catalysts. It was postulated that the dissociation of CO and the hydrogenation of surface carbon take place on metallic Rh sites while CO insertion occurs on the Rh in an oxidized state.^(29,32) Rendulic and Sexton⁽¹¹⁸⁾ have suggested that alcohols adsorb on transition metal surfaces, such as Pt, via interaction of the lone pair orbital of oxygen in the alcohols with the metal. Benziger and Madix⁽¹¹⁷⁾ have observed that ethanol is adsorbed as ethoxy on an Fe surface. One might speculate that an electronegative oxygen in the added ethanol may preferentially adsorb on Rh^+ sites to block the formation of oxygenated compounds. However, Ponec⁽⁸⁰⁾ has reported no correlation of the selectivity for C_2 oxygenates with the amount of Rh^+ present, in contrast to what have been found for Pd catalysts.⁽¹³⁸⁾ Katzer et al.⁽⁶⁾ reported from an XPS study that there was no evidence to support the existence of Rh^+ on Rh/TiO_2 , which is known to be active for the formation of C_{2+} oxygenates. Similar results have also been reported for $\text{Rh}/\text{La}_2\text{O}_3$ by Kuznetsov et al.⁽⁷⁵⁾. Although we are not able to determine the type of active site responsible for CO insertion at present, our results and several previous studies^(29,30) have shown that active sites for the formation of C_{2+} oxygenates are probably different from those for the formation of hydrocarbons.

In addition to a high activity and selectivity in the formation of ethanol, $\text{Rh}/\text{La}_2\text{O}_3$ exhibited a high activity and selectivity in

conversion of ethanol to methane and dehydration of ethanol. This suggests that the readsorption of ethanol on those sites for decomposition of ethanol did not occur to any noticeable extent during the synthesis.

Ethyl acetate is known to be a secondary product formed during CO hydrogenation over certain supported Rh catalysts.⁽²⁹⁾ However, an increase in the formation of ethyl acetate was not observed during the addition of ethanol in this study. In contrast to this result, we have observed that the addition of ethanol over Rh/SiO₂ leads to an increase in the formation of ethyl acetate (see Chapter 4). A similar result has also been reported for Mn-Mo-Rh/SiO₂.⁽²⁹⁾ This demonstrates that the support has a strong effect not only on the primary reactions but also on the secondary reactions over Rh catalysts.

6.3.2 Effect of Alkali Promotion

The major effects of the addition of alkali promoters on the catalytic properties of Rh/La₂O₃ were to decrease dehydration and dehydroxymethylation (conversion of ethanol to methane)⁽⁷⁹⁾ activities of ethanol for K and Cs-Rh/La₂O₃, to suppress hydrogenation, and to increase C₂ oxygenate selectivity for Li-Rh/La₂O₃ in CO hydrogenation. La₂O₃ (Table 6-7) is inactive in dehydration of ethanol and conversion of ethanol to methane and Rh is active in dehydration (see Table 4-4) so that the dehydration and conversion of ethanol to methane over Rh/La₂O₃ must be attributed to Rh. The

inability of K- and Cs-promoted Rh/La₂O₃ to catalyze dehydration of ethanol and conversion of ethanol to methane as shown in Table 6-7 seems to suggest that at least part of the K and Cs promoters are located on the Rh metal, poisoning dehydration of ethanol and conversion of ethanol to methane. Praliaud et al.⁽⁴⁴⁾ observed that K⁺ species on K-promoted Ni/SiO₂ exist on both the metal and the support.

The overall acidity of alkali-promoted Rh/La₂O₃ decreased in the order: Rh/La₂O₃, Li-Rh/La₂O₃ > K-Rh/La₂O₃, Cs-Rh/La₂O₃, as indicated by the activity of alcohol dehydration. It appears that there is no correlation of oxygenate selectivity to the acidity/basicity of alkali-promoted Rh/La₂O₃ and unpromoted Rh/La₂O₃ contrary to what was found for just supported Rh catalysts.⁽⁶⁾

The suppression of hydrogenation over alkali-promoted Rh/La₂O₃ is evidenced by an increase in the ratio of C₄=/C₄ (Table 6-8) and the decrease in the rates of ethylene and propylene hydrogenation (Table 6-5 and 6-6). The increase in olefin selectivity upon alkali promotion could be due to a decrease in the amount of adsorbed H and/or a diminution in the hydrogenation steps.⁽⁴⁵⁾ Moreover, the increase in CO adsorption energy brought about by alkali promotion⁽⁵⁵⁻⁵⁷⁾ may contribute to the suppression of hydrogenation since high coverages of CO or a surface carbide is known to decrease the rate of hydrogen adsorption. In addition to these factors, the decrease in the rate of conversion and the rate of hydrogenation for the added ethylene and propylene over K- and Cs-Rh/La₂O₃ could result

Table 6-8: Effect of Alkali Promoters on the Mole Ratio of Some Specific Products

	\bar{C}_2/C_2	\bar{C}_3/C_3	\bar{C}_4/C_4
Rh/La ₂ O ₃	1.69	3.95	5.76
Li-Rh/La ₂ O ₃	2.68	6.06	7.67
K-Rh/La ₂ O ₃	1.74	2.35	8.40
Cs-Rh/La ₂ O ₃	1.78	2.40	8.32

300°C, 1 atm and CO/H₂ = 1

from the suppression of olefin adsorption. Shigehara and Ozaki⁽¹⁴⁰⁾ have found that the addition of potassium to Ni suppresses the irreversible adsorption (strong adsorption) of ethylene. It has been suggested that the adsorption of hydrocarbons such as ethylene on transition metals is associated with a charge transfer from the hydrocarbon to the metal.⁽¹⁴¹⁾ Zaera and Somorjai⁽¹⁴²⁾ have proposed that potassium on the metal surface, serving as an electron donor, could inhibit this charge transfer, making the adsorption of hydrocarbons less favorable.

As shown in Figure 3-1, the suppression of hydrogenation could increase the C₂ oxygenate selectivity and it could also decrease the overall activity of synthesis by inhibition of the formation of precursors such as CH_x. Thus, the promotion of CO insertion appears to be crucial for improving both the activity and the selectivity of the formation of C₂ oxygenates. The enhancement of CO insertion over Rh/La₂O₃ brought about by the Li promoter (Tables 6-4 and 6-5) seems to be involved with both the Li promoter and the La₂O₃ support because this promotion was not observed for other similar studies using Rh/TiO₂ (Chapter 5), Rh/MgO, Rh/Al₂O₃, and Rh/SiO₂ (Chapter 7) under the same reaction conditions. It has been suggested that La species may migrate onto Pd during hydrogen reduction of Pd/La₂O₃ at 400°C forming small patches on the Pd metal particles.⁽¹⁴³⁾ It is still not clear whether this migration of La species can occur in a Rh system. However, there is a possibility that both Li and La species could form small patches on Rh metal particle resulting in a metal-alkali

promoter-support interaction. Further characterization of these catalysts is required to verify this interaction.

6.4 Conclusions

This study has demonstrated that the ability for synthesis of C_2 oxygenates during CO hydrogenation is closely related to the ability for synthesis of C_3 oxygenates during the reaction of C_2H_4 with CO/ H_2 . It also confirms the reaction scheme (Figure 3-1) for the synthesis of hydrocarbons and oxygenates as proposed in Chapter 3. The active sites for the formation of oxygenates appear to be different from those for the formation of hydrocarbons. The selectivity and activity of a Rh catalyst is dependent upon its ability to catalyze those specific reaction steps such as CO dissociation, hydrogenation and CO insertion. These specific reaction steps have been found to be strongly dependent upon the type of alkali promoter.

The overall effect of alkali promoters on Rh/ La_2O_3 in the synthesis of oxygenated compounds can be summarized as follows:

- Li-promotion enhances CO insertion reaction and slightly affects hydrogenation on Rh/ La_2O_3 , resulting in increases in both selectivity and formation rate of C_2 oxygenated compounds during CO hydrogenation. It also increases both selectivity and formation rate of C_3 oxygenated compounds during the reaction of ethylene with CO/ H_2 .

- K or Cs promotion suppresses both CO insertion and hydrogenation on Rh/La₂O₃ resulting in decreases in selectivity and activity to oxygenated compounds and a decrease in overall activity.