7.0 THE COMBINED EFFECTS OF ALKALI PROMOTERS AND SUPPORTS ON THE SYNTHESIS OF OXYGENATED COMPOUNDS OVER RHODIUM CATALYSTS

7.1 Background

The synthesis of oxygenated compounds over supported Rh catalysts is very sensitive to the presence of alkali promters. Previous studies on alkali-promoted Rh/TiO_2 and Rh/La_2O_3 have suggested that alkali promoters may distribute themselves on both the metal and support surfaces resulting in a modification in the properties of the catalysts. The observed effect of alkali promotion on oxygenate synthesis over supported Rh catalysts appears to result from a combined effect of promoter and support. This complex effect can be described schematically in Figure 7-1. Alkali species may interact directly with surface reactive intermediates to provide special sites for adsorption.(139) It may locate on metal surface resulting in modification of the states and properties of that surface. Another possible effect is that promoters may alter the properties of the support. This alteration could, in turn, change the catalytic behavior of the metal.

The present chapter considered the combined effects of alkali promoters and supports on the catalytic behavior of Rh catalysts. The catalysts utilized for this study included both unpromoted and alkali-promoted Rh black, Rh/Al_2O_3, Rh/TiO_2, Rh/SiO_2, Rh/La_2O_3, and Rh/MgO.

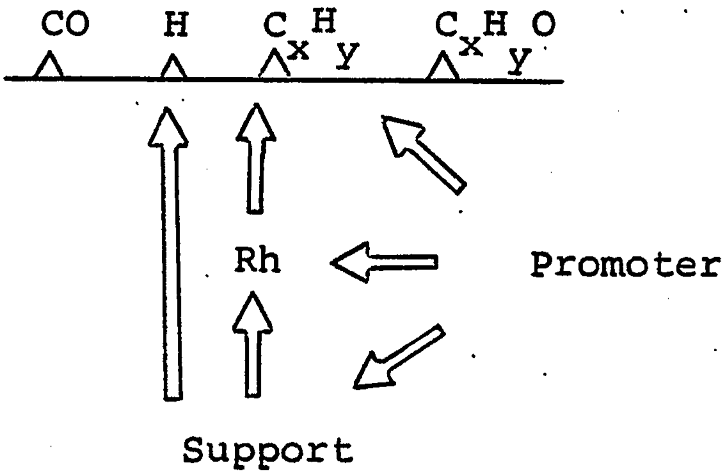

Figure 7-1 Schematic Diagram of Effect of Alkali Promotion on Supported Rh

7.2 Results

7.2.1 Rh and Li-Rh

In order to understand the complexity of metal-promoter-support interactions, it is important to consider first Li-promoted Rh black as reference catalyst. Table 7-1 shows product distributions from CO hydrogenation over these two catalysts. Li-promoted Rh exhibited a higher activity and selectivity for the formation of C_{2+} oxygenated compounds. Li-promotion appears to enhance the formation of C_{2+} oxygenates at the expense of the formation of C_{2+} hydrocarbons. Table 7-2 lists results of the addition of probe reactants to CO/H_2. Li-promoted catalyst showed a lower rate of ethylene conversion and a lower selectivity for the formation of ethane in comparison with unpromoted catalyst. An increase in selectivity to C_3 oxygenated compounds over the Li-promoted catalyst appears to be due to the suppression of hydrogenation rather than an enhancement of CO insertion activity. Ethanol addition to CO/H_2 over Rh black resulted in the formation of C_2 hydrocarbons. The doping of Li on Rh black promoted the conversion of ethanol to methane and the incorporation of ethanol into C_3 oxygenated compounds but inhibited the dehydration of ethanol to C_2 hydrocarbons. In the case of acetaldehyde addition, ethanol and C_2 hydrocarbons were observed to be major products. Li promoters partly suppressed conversion of acetaldehyde to C_2 hydrocarbons.

Table 7-1 Effect of Li on CO Hydrogenation over Rh Black

Catalysts	Rate of CO Conv. mole/kg/hr	Selectivity (wt%)					
		C_1	C_{2+}	MeOH	MeCHO	ETOH	C_3OX
Rh black	0.487	10.9	47.3	15.1	3.2	23.2	0
Li-Rh black	1.7	16.2	20.8	14.2	8.9	32.6	6.4

Table 7-2 Product Selectivity from Probe Molecule (C_2H_4, EtOH and MeCHO) Reaction During CO Hydrogenation over Rh black and Li-Rh black

Catalysts	Probe Reactant	Rate of Probe Reactant Conv. (mole/kg/hr)	Selectivity (mole %)							
			C_1	C_2	C_{3+}	MeOH	MeCHO	EtOH	C_3OX	C_4OX
Rh	3 mole % C_2H_4	6.42	0	76.2*	0.3	0	0	0	23.5	0
Li-Rh	3.5 mole % C_2H_4	1.72	0	61.5*	0.5	0	0	0	38.3	0
Rh	0.9 mole % EtOH	0.12	0	8.7	0	0	91.3	-	0	0
Li-Rh	1.3 mole % EtOH	0.13	22	0	0	0	64.3	-	10.8	2.7
Rh	2.2 mole % MeCHO	17.5	0.8	63.4	0	0	-	12.9	2.2	0.3
Li-Rh	3.4 mole % MeCHO	7.8	0.4	49.4	0	0	-	47.2	2.3	0

*$C_2 = C_2H_6$

7.2.2 Alkali-Promoted Rh Catalysts

Figure 7-2 shows the dependence of activity for CO conversion on the types of alkali promoter and support. The activity for CO conversion decreased in the order: *unpromoted > Li > K > Cs* for TiO_2, SiO_2, and MgO-supported Rh catalysts. In contrast, alkali promotion seemed to have little effect on CO conversion over Al_2O_3-supported Rh catalysts. The combined effects of alkali promoters and supports on C_2 oxygenate selectivity and CH_4 and C_{2+} hydrocarbon selectivity are represented in Figure 7-3 and Table 7-3, respectively. The effect of alkali promotion is strongly dependent on the type of support used. In the case of Rh/TiO_2, alkali promotion enhanced the selectivity to C_2 oxygenated compounds while reverse effect was observed for Rh/SiO_2. For Rh/La_2O_3 and Rh/MgO, the trend of alkali promotion is less obvious.

Results of ethylene addition to CO/H_2 over these promoted and unpromoted catalysts are shown in Figure 7-4 and Figure 7-5. Except in the case of Rh/Al_2O_3, alkali promotion uniformly decreased the rate of conversion of ethylene. The selectivity to C_3 oxygenated compounds was somewhat enhanced by the presence of alkali promoters. This increase in C_3 oxygenated compounds appears to be due to a strong suppression of hydrogenation rather than an increase in CO insertion activity.

Ethanol addition to CO/H_2 was studied over Rh/Al_2O_3, Rh/SiO_2 and Rh/La_2O_3 (Table 7-4, Table 7-5, and Table 6-7). The suppression of ethanol dehydration was identified as major effect of alkali promotion

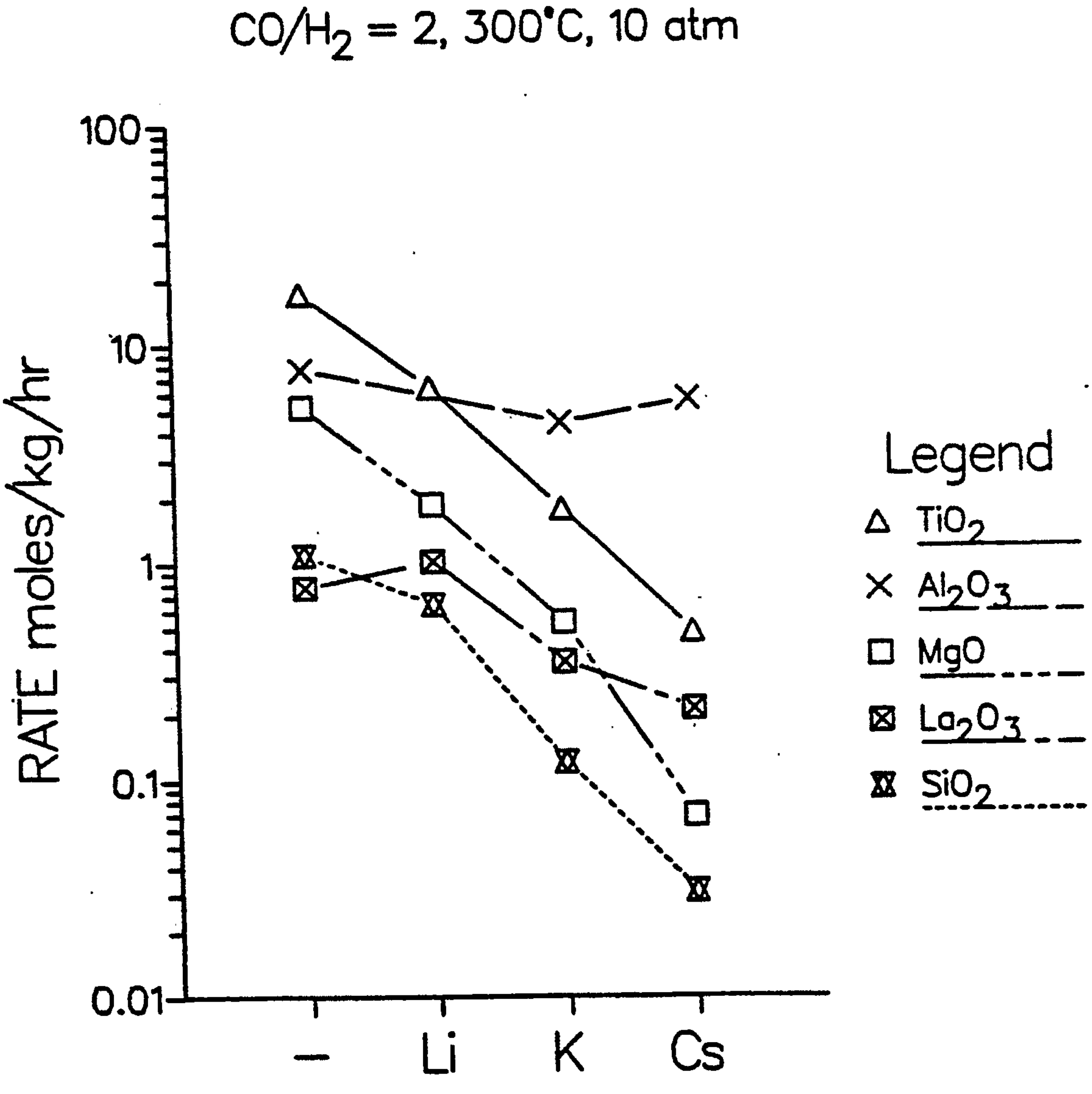

Figure 7-2 Effects of Alkali Promoters and Supports on the Activity of CO Conversion

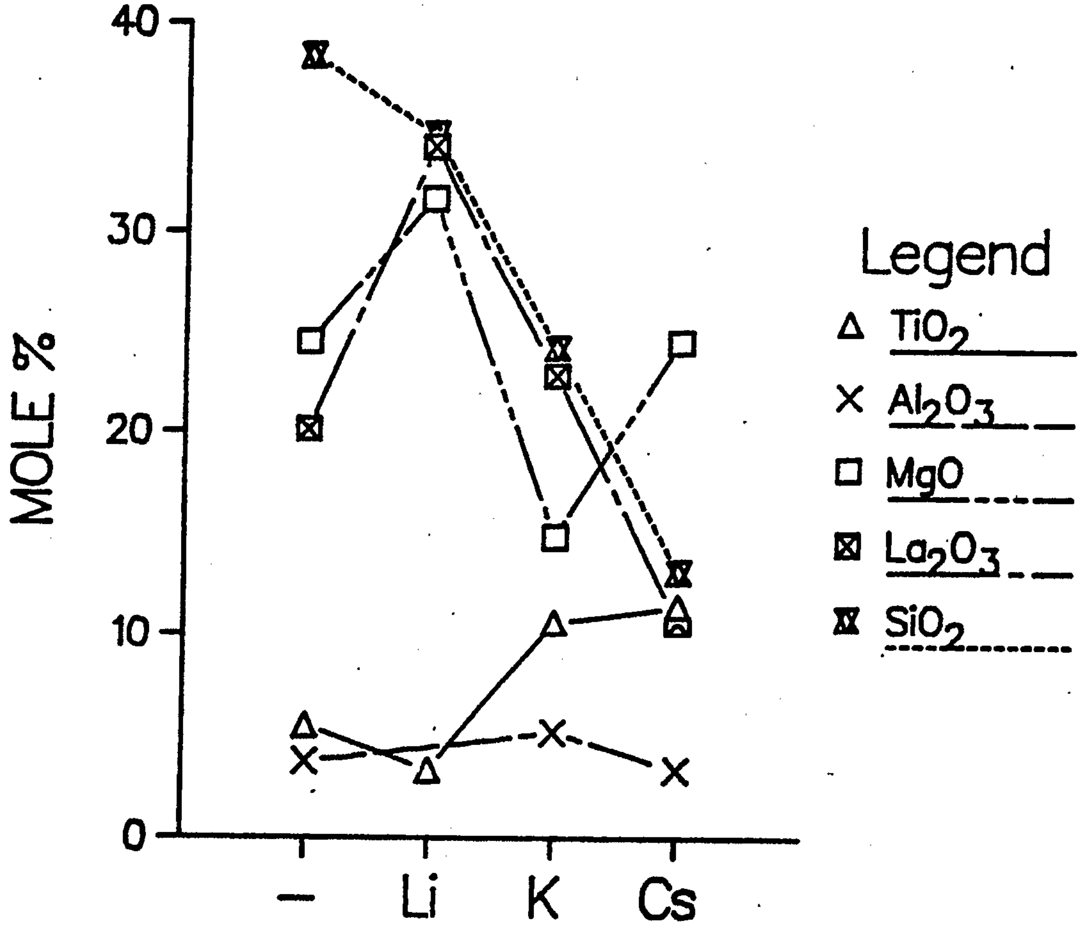

Figure 7-3 Effects of Alkali Promoters and Supports on C_2 Oxygenate Selectivity during CO Hydrogenation

Table 7-3 Effect of Alkali Promoters and Supports on CH_4 and $C_{2+}HC$ Selectivities during CO Hydrogenation

Catalysts		Selectivity (mole%)			
		-	Li	K	Cs
Rh/Al_2O_3	CH_4	86.9	81.7	83.4	86
	$C_{2+}HC$	6.4	12.7	8.5	8.5
Rh/TiO_2	CH_4	74.8	71.9	65.6	42.4
	$C_{2+}HC$	17.0	17.3	10.5	30.5
Rh/SiO_2	CH_4	45	37.3	39.8	33.3
	$C_{2+}HC$	7.8	13.5	25.0	45.8
Rh/La_2O_3	CH_4	42.5	22.68	29.0	45.6
	$C_{2+}HC$	14.1	19.8	18.9	23.9
Rh/MgO	CH_4	34.2	25.7	34.6	34.1
	$C_{2+}HC$	27.3	32.9	45.9	27.2

HC = Hydrocarbons

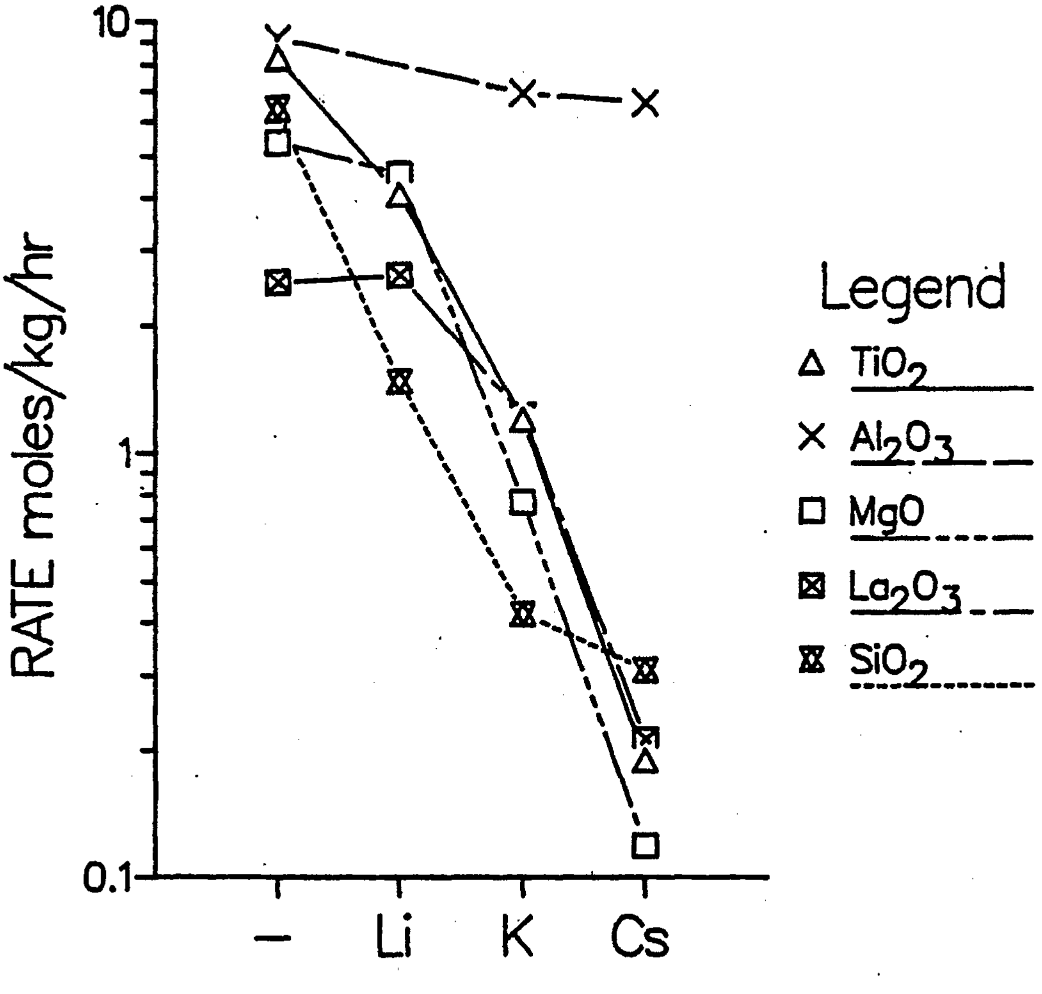

Figure 7-4 Effects of Alkali Promoters and Supports on the Rate of Conversion of Ethylene Added during CO Hydrogenation

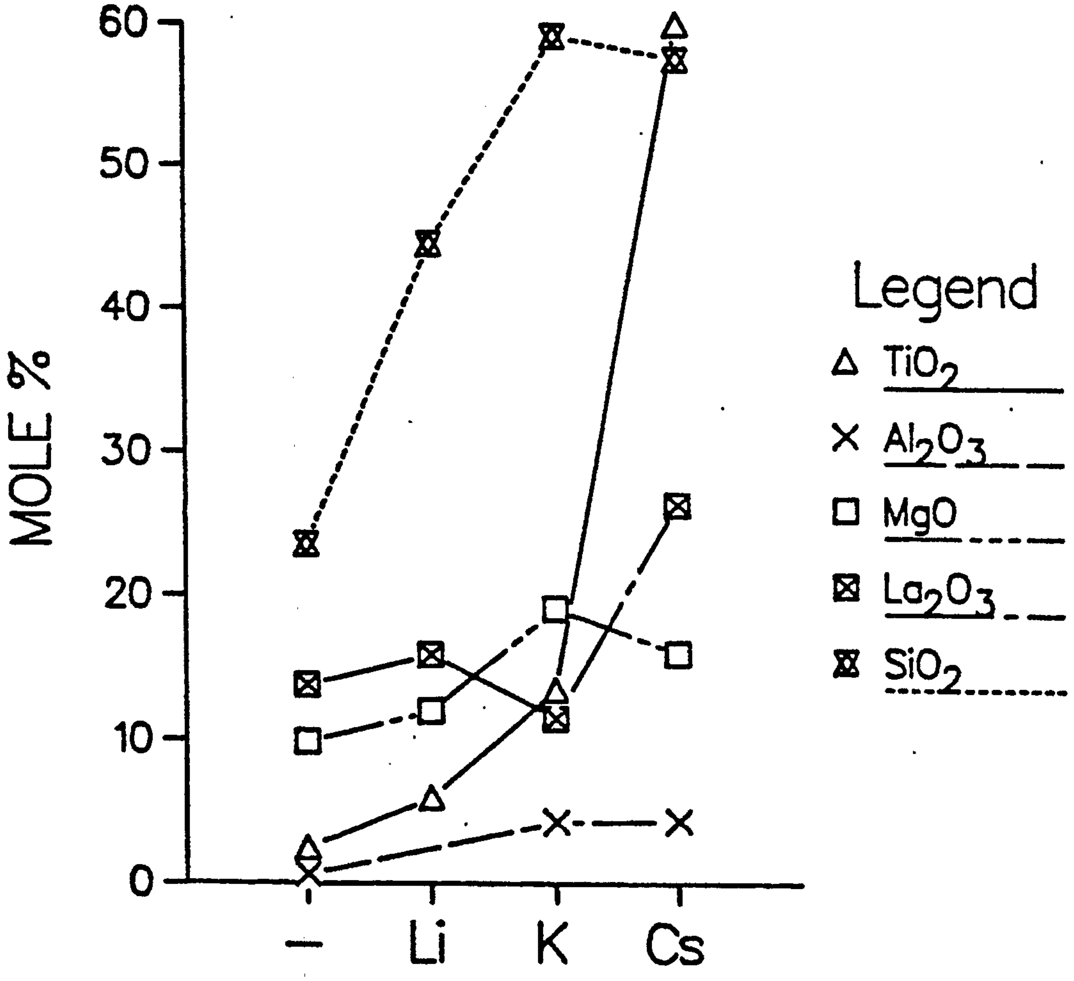

Figure 7-5 Effects of Alkali Promoters and Supports on C_3 Oxygenate Selectivity from Ethylene Reaction during CO Hydrogenation

Table 7-4 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Rh/SiO_2 and Alkali-Promoted Rh/SiO_2

Catalysts	Rh/SiO_2	Li-Rh/SiO_2	K-Rh/SiO_2
Amounts of EtOH Added in CO/H_2 mol%	0.65	0.45	0.48
Rate of EtOH conversion mole/kg/hr	0.28	0.41	0.26
Selectivity mole %			
CH_4	15.1	20	53.2
C_2	2.1	8.6	2.6
C_{3+}	3.0	4.6	3.8
MeOH	6	6	0
MeCHO	20.8	14	21.6
C_3 oxgy.	38.6	38.5	1
EtOAc	14	8.3	17.8

300°C, 10 atm, CO/H_2 = 1

Table 7-5 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Rh/Al_2O_3 and Alkali-Promoted Rh/Al_2O_3

Catalyst	Rh/Al_2O_3	$Li-Rh/Al_2O_3$	$K-Rh/Al_2O_3$	$Cs-Rh/Al_2O_3$
Amount of EtOH added %	0.3	0.5	0.6	0.1
Rate of EtOH Conversion (mole/kg/hr)	0.118	0.184	0	0
Selectivity mole %				
CH_4	0	0	0	0
C_2	16.9	10.8	0	0
$C_{3+}HC$	16.9	38	0	0
MeOH	0	0	0	0
MeCHO	35.5	14.1	0	0
C_3OX	3.3	0.5	0	0
EtOAc	27.1	35.4	0	0

on ethanol reaction over Rh/Al_2O_3 and Rh/La_2O_3. This effect was not observed for Rh/SiO_2 since this catalyst is not active for ethanol dehydration.

The incorporation of ethanol into C_3 oxygenated products took place on Rh/SiO_2 and $Li\text{-}Rh/SiO_2$ catalysts. As discussed in Chapter 3, several mechanisms have been proposed to explain this specific reaction step. At present, it is still not clear what is the predominant route for the incorporation of ethanol to C_3 oxygenated compounds.

7.3 Discussion

Due to the complexity of the combined effects of alkali promoters and supports, it is important to study the effect of alkali promotion on Rh metal and the effect of supports on Rh metal separately. The effects of the alkali promoter, Li, on CO hydrogenation over Rh metals were identified to cause the following: (a) increased CO hydrogenation activity, (b) decreased ethylene hydrogenation activity, (c) increased selectivity for CO insertion, (d) enhanced incorporation of ethanol into C_3 oxygenated compounds, and (e) decreased activity for dehydration of ethanol. The effect of the support on C_2 oxygenate selectivity essentially parallels to that of the support on the CO insertion selectivity. It increased in the order: $Al_2O_3 < TiO_2 <$ MgO, $La_2O_3 < SiO_2$. It is apparent that the combined effects of alkali promoters and supports are not the superposition of both effects. This may be due to the fact that both effects are chemical in nature. In addition, other effects, such as the creation of active sites(62,139) and effects brought about by modification of support by alkali promoters, may play an important role in this complex effect.

The most obvious common effects of alkali promotion on supported Rh catalysts are suppression of ethylene hydrogenation and ethanol dehydration. These two effects may be attributed to a direct interaction between metal and alkali promoters since these effects were identified as major effects of alkali promotion on Rh black. The suppression of ethanol dehydration suggests that alkali promoters decrease the acidity of the catalyst. Comparing ethanol dehydration activity (Table 6-7, 7-4 and 7-5) with CO hydrogenation selectivity (Figure 7-3 and Table 7-3), it appears that there is no direct correlation between acidity/basicity of supported Rh catalysts and CO hydrogenation selectivity. A similar observation has also been reported by van den Berg.(29)

On the basis of the reaction (Figure 3-1) scheme proposed in Chapter 3, the suppression of hydrogenation would result in an enhancement of selectivity for CO insertion to form C_{2+} oxygenated compounds and CH_x insertion to form higher hydrocarbons, and it may also cause a decrease in CO hydrogenation activity. It is important to note that alkali promoters suppress the rate of formation of all the products, except in the cases of Li-Rh and Li-Rh/La_2O_3 catalysts. The selectivity for CO insertion or CH_x insertion is strongly dependent on the type of support and alkali promoter. In the case of Rh/TiO_2 which demonstrated a higher selectivity for the formation of higher hydrocarbons than that of C_2 oxygenated compounds, the addition of alkali promoters enhanced the selectivity for C_2 oxygenate formation. On the other hand, Rh/SiO_2 exhibited a high selectivity for C_2 oxygenate formation. Alkali promotion shifted the selectivity to C_{2+} hydrocarbons. This shift in selectivity from one product to another product is mainly due to a stronger suppression of formation of one product over that of another.

The absence of an effect of alkali promotion on CO hydrogenation over Rh/Al_2O_3 catlaysts would seem to be due to a strong affinity of the basic alkali promoters with the acidic support resulting in most of added alkali promoter being situated on the support. The difference in the effect of alkali promotion on CO conversion activity between Rh black and supported Rh is possibly related to their CO dissociation activity. Rh metal itself is not very active for CO dissociation(21) while supports(68) and alkali promoters(56) are known to promote CO dissociation. Promotion of CO dissociation on Rh metal may result in a high activity for CO conversion while enhancement of CO dissociation over a supported Rh catalyst, which is active for CO dissociation, may cause an excess of surface carbon leading to decrease in activity. In addition, Rh black and supported Rh catalysts have a dramatic difference in metal particle size. This could be another factor contributing to this difference.

Li promotion results in an increase in the activity for incorporation of ethanol into C_3 oxygenated compounds on Rh black. This promotion was also observed to occur on Rh/SiO_2. Since the mechanism for this incorporation reaction is not clear, the effect of alkali promotion on this reaction is far from being understood and it must await further investigation.

7.4 Conclusions

Suppression of hydrogenation and ethanol dehydration was identified as major effects of alkali promotion. CO insertion was found to be dependent upon both the alkali promoter and the support.

The combined effects of promoters and supports are not simply the superposition of these two effects. Factors such as metal particle size, distribution of alkali promoters on the support and metal surfaces, and modification of the support by alkali promoters may complicate this metal-promoter-support interaction.

8.0 EFFECT OF POTASSIUM PROMOTERS ON METHANOL SYNTHESIS OVER Pd/SiO_2

8.1 Background

It is well known that Pd is a good catalyst for the selective synthesis of methanol under high pressures. Addition of alkali promoters to Pd catalysts produced a marked modification in the selectivity for methanol synthesis.(48) Although the effects of alkali promoters have been identified, the mechanisms of these effects are unclear. In the present work, a series of K-promoted Pd/SiO_2 have been studied to help elucidate the role of potassium on methanol synthesis.

8.2 Results

The metal particle sizes of these supported metal catalysts were determined by static hydrogen chemisorption at 25°C(146) and X-ray diffraction using a MoKα radiation source. The results are shown in Table 8-1. Due to suppression of hydrogen chemisorption brought about by potassium promotion, hydrogen chemisorption appears to be inappropriate for measuring average metal particle size in these alkali-promoted catalysts.(146)

8.2.1 Pd/SiO_2 and K-Pd/SiO_2

Due to uncertainty in measuring the number of surface atoms for alkali-promoted catalysts(146) and to the fact that selectivity is the

Table 8-1 The Average Metal Particle Sizes of Pd/SiO_2, $K\text{-}Pd/SiO_2$

Catalysts	Average Metal Particle Size (Å)
Pd/SiO_2	$41^{(a)}$ $< 40^{(b)}$
$K\text{-}Pd/SiO_2$ (K/Pd = 0.6)	$87.3^{(a)}$ $< 40^{(b)}$
$K\text{-}Pd/SiO_2$ (K/Pd = 1.8)	$140^{(a)}$ $< 40^{(b)}$

(a) Determined by static hydrogen chemisorption at 25°C, $H_{irr}/Pd = 1$.

(b) Estimated by X-ray diffraction using MoKα property of interest, the activity of these catalysts for methanol synthesis is expressed in mole/kg/hr. The product distribution for CO hydrogenation over Pd/SiO_2, K-Pd/SiO_2 is shown in Table 8-2. Pd/SiO_2 demonstrated a very high selectivity for methanol formation. The addition of K promoters to Pd/SiO_2 resulted in decreases in both the selectivity and the activity for methanol formation while it increased the activity and selectivity for the formation of methane and higher hydrocarbons.

8.2.2 Addition of Ethylene to CO/H_2

In order to determine the effect of potassium promoters on the hydrogenation ability of these catalysts, a small amount of an unsaturated hydrocarbon (ethylene) was added to the CO/H_2 reactant stream. The added ethylene, CO, and H_2 may compete with one another for the same active sites. In addition, the added ethylene may interact with intermediates produced from CO hydrogenation.(85) The product distributions from reaction of the added ethylene over Pd/SiO_2 and K-Pd/SiO_2 is shown in Tables 8-3. It is interesting to note that the addition of ethylene results in a decrease in methanol formation for Pd/SiO_2 and K-Pd/SiO_2. The extent of suppression of methanol formation seems to parallel the activity of methanol formation of these catalysts (Tables 8-2 and 8-3).

The addition of potassium promoters to Pd/SiO_2 resulted in a decrease in rate of ethylene hydrogenation while it slightly increased the rate of formation of C_3 oxygenated compounds.

Table 8-2 Product Selectivity during CO Hydrogenation over Pd/SiO_2 and K-Pd/SiO_2

Atom Ratio of K to Pd	0	0.6	1.8
r_{CO} (moles/kg/hr)	2.7	0.534	0.38
Selectivity (wt%)			
CH_4	0.4	3.9	12.5
C_{2+} HC	2.3	36.0	42.0
MeOH	97.3	60.1	40.7
C_2 OX	0	0	4.8
Activity (mole/kg/hr)			
CH_4	0.023	0.028	0.056
C_{2+}HC	0.051	0.092	0.091
MeOH	2.5	0.216	0.09
C_2OX	0	0	0.008

300°C, 10 atm., $CO/H_2 = 1$, 2.3 wt% Pd/SiO_2

Table 8-3 Product Selectivity from Ethylene Reaction During CO Hydrogenation over Pd/SiO_2 and $K-Pd/SiO_2$

Atom Ratio of K to Pd	0	0.6	1.8
r_{CO} during CO/H_2 (a)	2.7	0.53	0.38
R_{CO} during $CO/H_2/C_2H_4$ (a)	1.75	0.66	0.55
$r_{C_2^=}$ (a)	36.17	35.0	5.8
Conversion of $C_2^=$ %	99	90	16.1
Selectivity (mole %)			
CH_4	0	0	0
C_2H_6	99.5	95.5	96.5
C_3+	0.3	0.1	0.5
C_3 OX	0.2	0.4	3.0
Change in r_{CH_3OH} during addition C_2H_4	-1.1	-0.032	-0.005
(%)	57	14.8	5

3.3 ~ 3.5 mole % in $CO/H_2 = 1$, 300°C, 10 atm.
(a) All rates are expressed in mole/kg/hr

8.3 DISCUSSION

The most interesting point of this study is the product distribution from reaction of ethylene added during CO hydrogenation obtained for Pd/SiO_2 and K-Pd/SiO_2 (Table 8-3). The results of adding ethylene were a significant suppression of the formation of methanol during CO hydrogenation over these catalysts while there was little effect on methane formation. This clearly suggests that (a) part of the adsorbed ethylene competed with CO for the same hydrogenation sites, (b) active sites for the formation of methanol are different from those for the formation of methane. Similiar suppression in methanol formation during the addition of 1-hexene to CO/H_2 over Cu/ZnO has been reported by Vedage and Klier.(147) They suggested that CO and 1-hexene compete for the same active sites resulting in this suppression.

Addition of a potassium promoter to Pd/SiO_2 caused a marked decrease in activity and selectivity for methanol formation while it increased the activity and selectivity for the formation of both methane and higher hydrocarbons. The presence of this potassium promoter also caused a suppression of ethylene hydrogenation during the addition of C_2H_4 to the CO/H_2 reactant stream. It seems to suggest that potassium promoters may preferentially block the active sites for methanol synthesis and ethylene hydrogenation over Pd/SiO_2. However, the effect of alkali promotion is generally considered to be electronic in nature.(43-45) If the electronic factor play a major role in the effect of alkali promotion, such similar suppression of activities for these two reactions suggests that some steps of these two reactions take place on the same active sites or at least on sites which have similar chemical properties. These active sites are subject to modification brought about by alkali promotion. This is somewhat confirmed by the fact that the rate of methanol formation decreases so significantly upon the addition of ethylene, suggesting competition for the same sites. It also suggests that not only CO hydrogenation to methanol but also at least most of ethylene hydrogenation take place on different active sites than methane formation.

There still exists controversy concerning the nature of active sites responsible for the formation of methanol. The formation of methanol has been suggested to take place (a) on Pd ions(62), (b) on small sized crystallites of Pd metal(144), (c) more actively on Pd (100) than on Pd (111)(81), (d) at the interface of Pd metal and the support.(48)

While we are still not able to differentiate what type of active sites is responsible for the methanol formation, it can be suggested that active sites for methanol formation are different from those for methane formation. Fajula et al.(144) have observed that the formation of methane over supported Pd catalysts is directly related to the density of acidic sites at the surface of the support. Accordingly, the addition of potassium to Pd/SiO_2 should decrease the acidity of the catalysts(142) so that the formation of methane would also decrease. On the contrary, an enhancement of methane and hydrocarbon formation was observed for potassium promoted Pd/SiO_2. Fajula et al.(144) have also pointed out that the formation of methane via CO dissociation followed by hydrogenation of resulting surface carbon can not definitely be ruled out for Pd catalysts. They have further noted that, if this is the case, the reasons for their observed correlation is not apparent. K promoters are known to be effective in promoting CO dissociation.(43) In contrast, Mori et al.(69) have observed that the addition of alkali promoters to Pd/Al_2O_3 causes a shift in the wave number of adsorbed CO to a lower value in IR spectroscopy. They have suggested that alkali promoters, mostly located on the Al_2O_3 support, decrease the dissociation probability of CO on Pd/Al_2O_3. It is therefore not clear how alkali promoters modify CO dissociation activity of supported Pd catalysts. A further study on this issue would provide a better understanding of the alkali promotion effect on CO hydrogenation over Pd catalysts.

The major effect of alkali promoter on methanol synthesis over Pd/SiO_2 catalysts have been suggested to be

(a) a modification of active sites (interface of the metal and the support) by alkali promoters(48),

(b) stabilization of some ions (assumed to be active sites for methanol formation) by the alkali promoters against reduction in a hydrogen atmosphere(62),

(c) creation of a defect structure which is improve the activity for the catalyst.(62)

All these propositions appear to indicate that alkali promoters are effective in promoting methanol formation. Kikuzono et al.(48) have observed that Li and Na cations promote methanol formation over Pd/SiO_2 while K and Cs cations decrease it. Klier(99) has found that Cs promoters suppress the methanol synthesis activity of Pd/SiO_2 but increase its activity for the water-gas-shift reaction. In contrast, Tatsumi et al.(145) have reported that methanol synthesis over Pd/SiO_2 was promoted when Li, Na, K, Rb, and Cs were used as promoters.

In this study, we found K^+ promotion (alkali promotion) to be effective in decreasing the hydrogenation ability of Pd/SiO_2 (suppressing CO hydrogenation to methanol and ethylene hydrogenation to ethane). Thus, alkali promoters appear to have two major effects on methanol synthesis which are opposite to each other. One effect is hydrogenation suppression which can decrease the activity of methanol synthesis. The other one is beneficial to the activity of active sites to activate CO or stabilize precursors to methanol.(48,62) Hence, the observed effect of alkali promotion on methanol synthesis may be due to the net effect of these two factors. A quantitative study of the effects of these two factors would be important for gaining a better understanding of alkali promotion on methanol synthesis.

8.4 Conclusions

The results of this study have suggested that the active sites for methanol formation are different from those for methane formation over Pd/SiO_2. Pd/SiO_2, which is active in methanol synthesis, showed a decrease in methanol formation during the addition of ethylene to the CO/H_2 reactant stream. The major effects of potassium promoters were identified to be (a) suppression of ethylene hydrogenation over Pd/SiO_2 and (b) suppression of hydrogenation of CO to methanol over Pd/SiO_2.

9.0 THE SYNTHESIS OF METHANOL ON Pd AND Rh CATALYSTS: A COMPARISON

9.1 Background

Pd, Pt, Ir, and Rh catalysts have been found to be active for methanol synthesis.(6,7,12,62,114,144,145) Although the mechanism for methanol synthesis over these catalysts is still not clear, the good methanol synthesis activities of these catalysts have been identified to be due to their high hydrogenation ability coupled with their ability to activate adsorbed CO nondissociatively.(7,71) Several recent studies have revealed that the selectivities and activities of Pd and Rh catalysts are greatly affected by the composition of the support(6,7) and the presence of promoters.(48) Pd supported on certain types of silica(144) exhibits high activity and selectivity for methanol formation. For Rh, even more basic supports(7,12) such as MgO and ZnO than those for Pd catalysts are required to promote the production of high yields of methanol while Rh on moderately basic supports (SiO_2 and La_2O_3) leads to good selectivity to ethanol. Some fundamental questions concerning methanol synthesis over these two metal catalysts still remain unanswered. Is the mechanism of methanol synthesis over Pd catalysts the same as that of methanol synthesis over Rh catalysts? What are the basic factors controlling the formation of methanol as opposed to the formation of ethanol?

This reports the results of a study of CO hydrogenation and the addition of probe molecules (ethylene and ethanol) to the CO/H_2 reactant stream over Pd/SiO_2, Rh black, Rh/SiO_2, Rh/La_2O_3, and

Rh/MgO. The objective was to compare the catalytic properties of Pd (which is active for methanol synthesis) and Rh catalysts (which are active for both methanol and ethanol synthesis) in order to better understand these syntheses.

9.2 Results

9.2.1 CO Hydrogenation

The metal particle sizes of these supported metal catalysts were determined by static hydrogen chemisorption at 25°C(146), H_2 TPD, and X-ray diffraction using a MoKα radiation source. The results are shown in Table 9-1. With the exception of Rh black, all these catalysts have comparable dispersions. Table 9-2 gives results for CO hydrogenation over Pd/SiO_2, Rh black, Rh/SiO_2, Rh/La_2O_3, Rh/MgO (reduced at 250°C) and Rh/MgO (reduced at 400°C). Activities are reported on a weight of catalyst basis due to the lack of knowledge of the fractions of the metal surfaces actually active and to the fact that selectivity in the parameter of concern for this study. As shown in Table 9-2, Pd/SiO_2 was very selective and active for methanol synthesis but inactive for C_2 oxygenate synthesis while Rh/SiO_2 was active for C_{2+} oxygenate synthesis but essentially inactive for methanol synthesis. In contrast, Rh black, Rh/La_2O_3, and Rh/MgO (reduced at 250°C) showed fair selectivities for both methanol and C_2 oxygenate synthesis. The product distributions over Rh/MgO appeared to be greatly affected by reduction temperature. Rh/MgO reduced at

Table 9-1 The Average Metal Particle Size of Pd and Rh Catalysts

Catalyst	Metal Particle Diameter (Å)			
	BET	H_2 TPD	H_2 G.V.	XRD
2.3% Pd/SiO_2	-	-	41	< 40
Rh Black	352	-	-	-
3% Rh/SiO_2	-	46	-	40
2.6% Rh/La_2O_3	-	27.5	-	< 30
2.3% Rh/MgO	-	-	52.9	< 30

Table 9-2 Activity and Product Selectivity During CO Hydrogenation over Pd and Rh Catalysts at 300°C

Catalyst	2.3 wt% Pd/SiO_2	Rh Black	3 wt% Rh/SiO_2	2.6 wt% Rh/La_2O_3	2.3 wt% Rh/MgO		
					(R250)*	R(400)*	(R400)
$-r_{CO}$ (moles/kg/hr)	2.7	0.48	1.3	0.77	0.254	0.50	5.23
Selectivity (mol%)							
CH_4	0.9	10.9	41.2	42.5	34.8	19.7	55.1
C_2HC	1.4	41.3	6.8	6.5	5.4	4.5	7.4
$C_{3+}HC$	0.4	6.3	1.8	7.4	4.3	4.6	10.0
MeOH	97.0	15.1	1.4	20.7	22.4	2.0	0.5
C_2OX	0	26.4	31.4	20.2	30.3	68.4	24.1
$C_{3+}OX$	0.1	0	16.6	2.7	2.8	0.7	2.9

*Reaction at 250°C
10 atm, $CO/H_2 = 1$, 300°C

250°C produced higher yields of methanol than that reduced at 400°C. The increase in reduction temperature, however, increased the rate of C_2 oxygenate (OX) formation.

9.2.2 Addition of Ethylene to CO/H_2

A small amount of ethylene (2.3 - 3% in CO/H_2) was added to the CO/H_2 reactant stream over these catalysts to probe their catalytic properties. Figure 9-1 and Table 9-3 show results of ethylene addition over these catalysts. All of these catalysts exhibited relatively high activity and selectivity for ethylene hydrogenation compared with the selectivities for CO insertion and incorporation into higher hydrocarbons. In fact, both Rh and Pd have long been known to be good catalysts for hydrogenation of olefins.(113) The selectivity for CO insertion to form C_3 oxygenates decreased in the orde . Rh black, $Rh/SiO_2 > Rh/La_2O_3 > Rh/MgO > Pd/SiO_2$.

It is interesting to note that the addition of ethylene to CO/H_2 over Pd/SiO_2 and Rh/MgO (reduced at 250°C) resulted in significant decreases in the formation of methanol. A decrease in CO conversion was also observed for Pd/SiO_2 during addition of ethylene to CO/H_2. In contrast, an increase in CO conversion was found for Rh black, Rh/SiO_2, Rh/La_2O_3, and Rh/MgO during the addition of ethylene to CO/H_2.

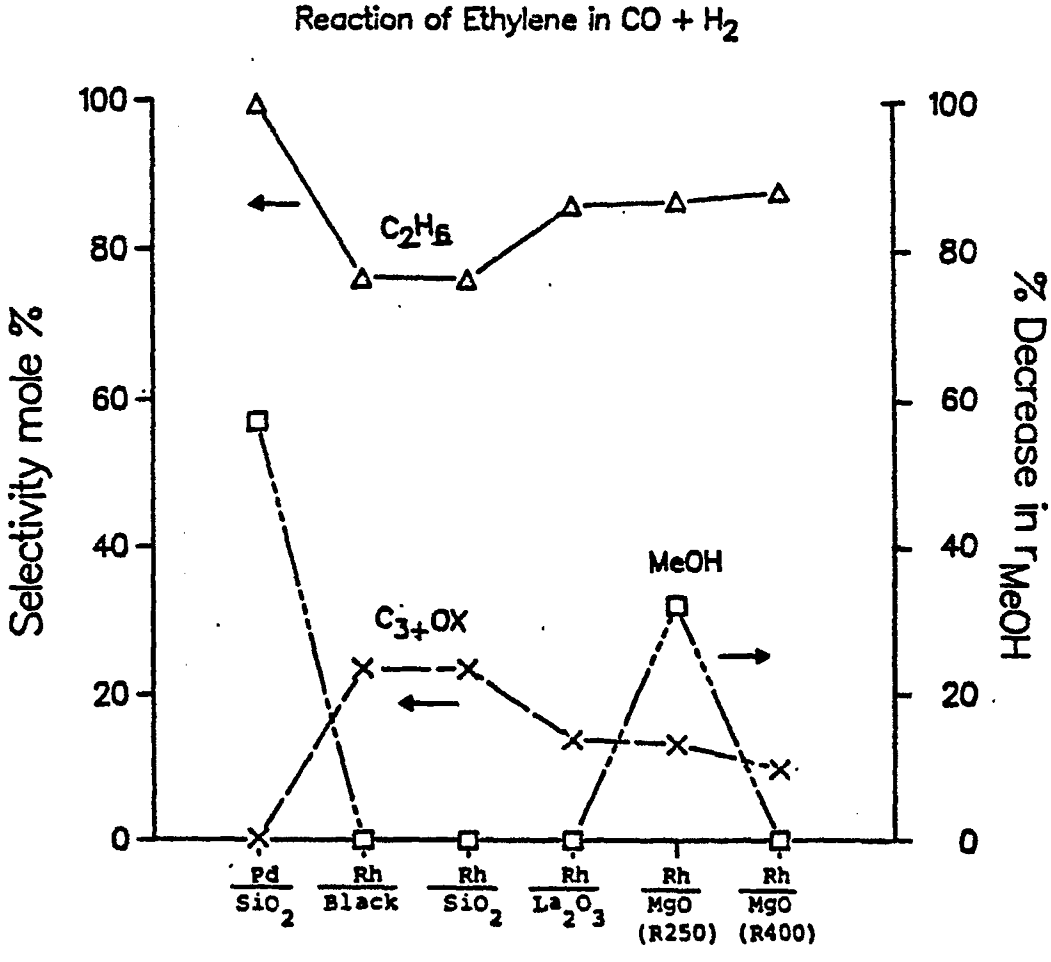

Figure 9-1 Product Selectivity from Ethylene Reaction during CO Hydrogenation over Pd and Rh Catalysts

Table 9-3 Product Selectivity from Ethylene Reaction During CO Hydrogenation over Pd and Rh Catalysts at 300°C

Catalyst	2.3 wt% Pd/SiO_2	Rh Black	3 wt% Rh/SiO_2	2.6 wt%** Rh/La_2O_3	2.3 wt% Rh/MgO	
					(R250)*	(R400)
$-r_{CO}$ (CO/H_2)	2.7	0.48	1.3	0.77	0.25	5.23
$-r_{CO}$($CO/H_2/C_2H_4$)	1.75	1.98	2.85	1.12	0.57	5.76
$-r_{C_2H_4}$	36.2	6.42	6.49	2.52	2.4	5.4
(% conv)	(99)	(71)	(71)	(32)	(27)	(61)
Selectivity (mol%)						
(From C_2H_4)						
CH_4	0	0	0	0	0	0
C_2H_6	99.5	76.2	76	85.8	86.3	87.6
C_{3+}	0.3	0.3	0.3	0.3	0.4	2.4
C_3OX	0.2	23.5	23.4	13.9	13.3	9.9
Δ (r_{MeOH})	-1.1	0	0	0	-0.012	0
during C_2H_4 add						
% change	-57	0	0	0	-32	0

All rates in mol/kg/hr

3% C_2H_4 in CO/H_2; 10 atm, CO/H_2=1 and 300°C

*Reaction at 250°C

**2.6% of C_2H_4 in CO/H_2

9.2.3 Addition of Ethanol to CO/H_2

The product distributions resulting from the added ethanol are shown in Table 9-4 and Figure 9-2 and 9-3. Pd/SiO_2 exhibited a very high selectivity for the dehydrogenation of ethanol while Rh/SiO_2 showed a much lower selectivity for this reaction but a high selectivity for the incorporation of ethanol into C_3 oxygenated compounds. This incorporation of ethanol into C_3 oxygenated compounds was also observed for Rh/MgO (R400). In contrast, Rh black and Rh/La_2O_3 were essentially inactive for this incorporation. Rh black demonstrated a high selectivity for the dehydrogenation of ethanol while Rh/La_2O_3 showed a high selectivity for conversion of ethanol to methane (dehydroxymethylation). In addition to the conversion of the added ethanol to this variety of hydrocarbon and oxygenated products, it is important to note that the added ethanol resulted in a suppression of methanol formation over Rh/La_2O_3. The promotion of methanol synthesis or conversion of ethanol to methanol over Rh/SiO_2 is not really significant given the low rate of formation.

9.3 Discussion

Pd/SiO_2, Rh black, Rh/SiO_2, Rh/La_2O_3, and Rh/MgO exhibited not only differences in CO hydrogenation selectivity but also variations in selectivities for reactions resulting from added ethylene and from added ethanol. Rh black, Rh/SiO_2, Rh/La_2O_3, and Rh/MgO, which were active for catalyzing the formation of C_2 oxygenated compounds during

Table 9-4 Product Selectivity from Ethanol Reaction During CO Hydrogenation at 300°C

Catalyst	2.3 wt% Pd/SiO_2	Rh Black	3 wt% Rh/SiO_2	2.6 wt% Rh/La_2O_3	2.3 wt% Rh/MgO	
					(R250)	(R400)
$-r_{CO}$ (CO/H_2)	1.24	0.48	1.10	0.77	-	5.23
$-r_{CO}$ ($CO/H_2/EtOH$)	1.67	0.36	1.24	0.75	-	4.16
% EtOH in CO/H_2	0.85	0.9	0.65	0.11	-	0.45
$-r_{EtOH}$	0.54	0.12	0.28	0.27	-	0.095
(% conv)	(6%)	(1.1%)	(16%)	(81%)	-	(7.2%)
Selectivity (mol%)						
(From EtOH)						
CH_4	0.7	0	15.1	84	-	27.2
C_2	4.2	8.7	2.1	6	-	0
C_{3+}	3.3	0	3.0	9	-	0
MeOH	0	0	6.0	-	-	0
MeCHO	87.6	91.3	20.8	0.5	-	52.4
C_3OX	2.6	0	38.6	0.5	-	20
$C_{4+}OX$	2	0	14.0	0	-	0.4
$\Delta(r_{MeOH})$	0	0	+0.017	-0.06	-	0
during EtOH add.						
% change	0	0	+21.5	-39	-	0

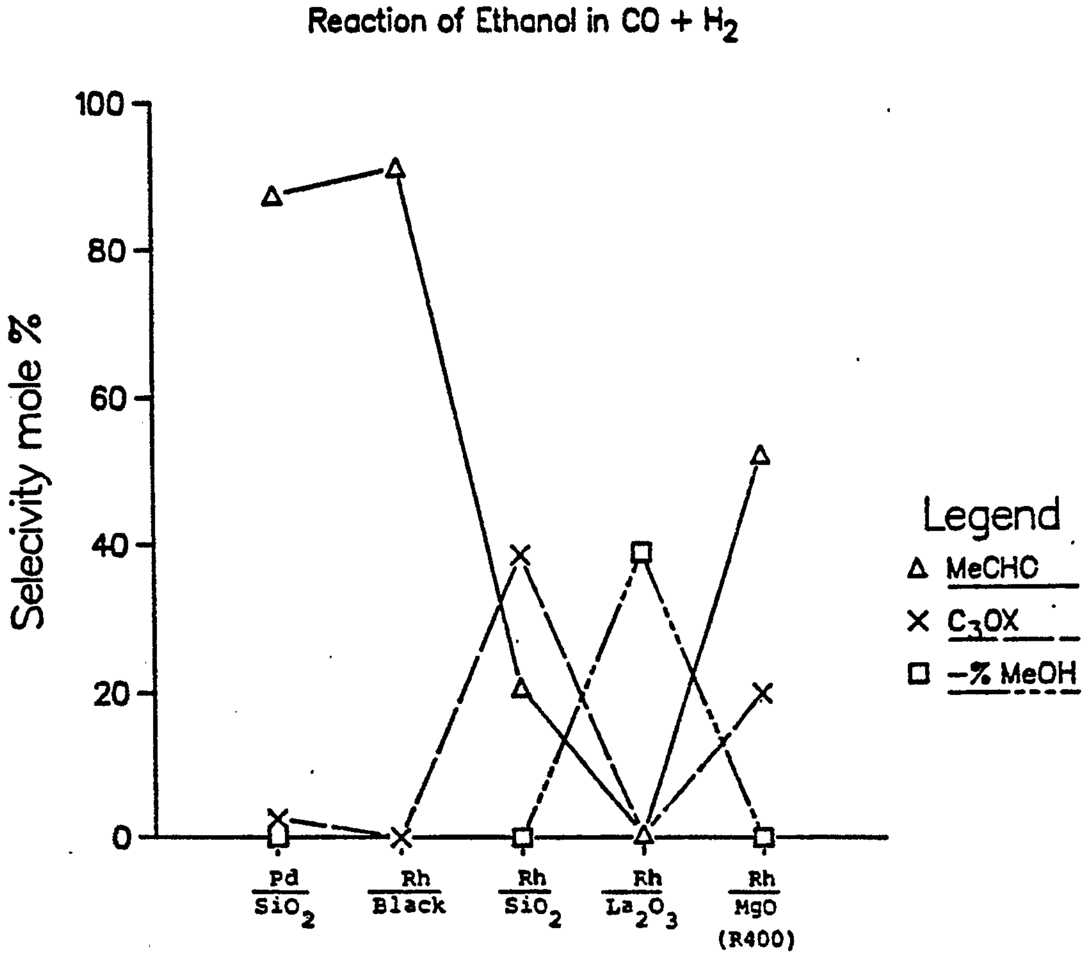

Figure 9-2 Oxygenate Selectivity from Ethanol Reaction during CO Hydrogenation over Pd and Rh Catalysts

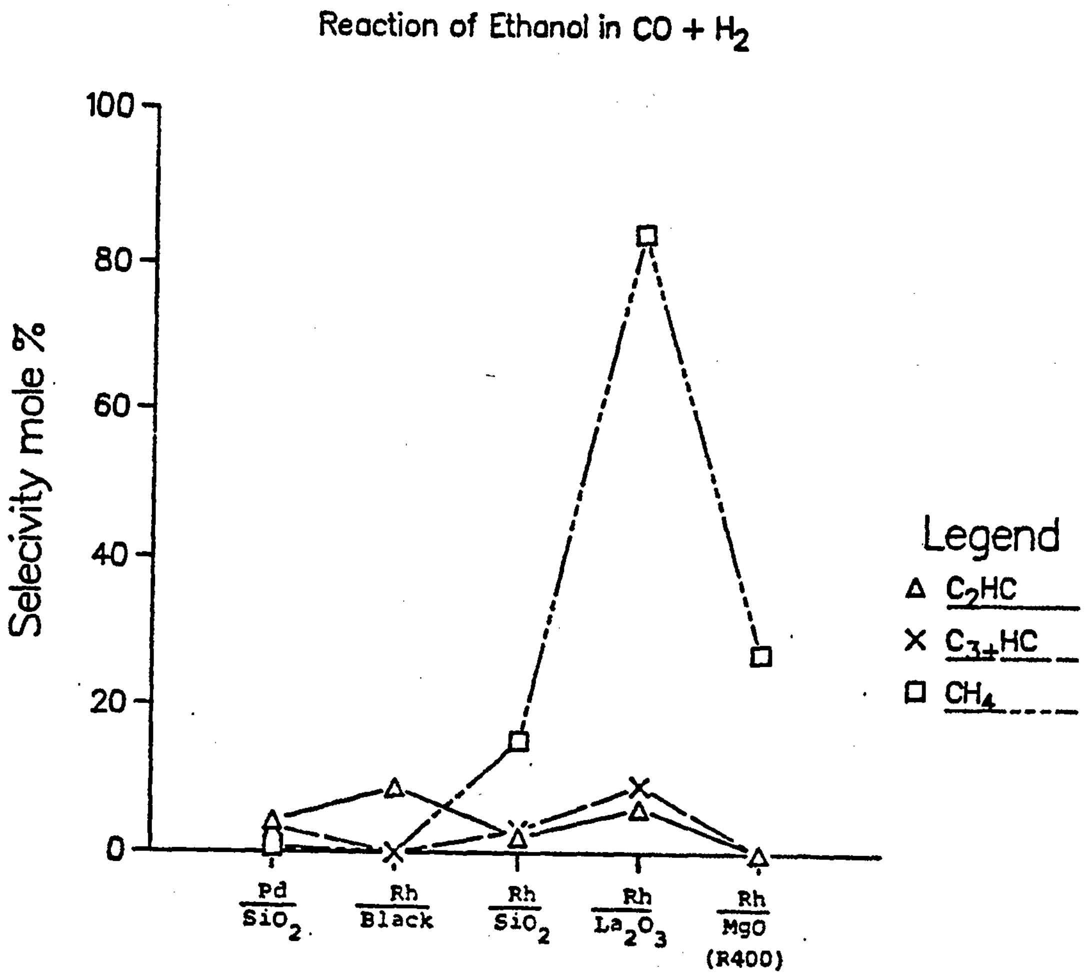

Figure 9-3 Hydrocarbon Selectivity from Ethanol Reaction during CO Hydrogenation over Pd and Rh Catalysts

CO hydrogenation, were active for catalyzing the formation of C_3 oxygenated compounds during the addition of ethylene to CO/H_2. As stated in Chapter 3, C_2 oxygenates have been shown to form from the insertion of CO into adsorbed CH_x which is generated by CO dissociation followed by hydrogenation during CO hydrogenation. Formation of C_3 oxygenates during the addition of ethylene to CO/H_2 has been suggested to result from the insertion of CO into adsorbed C_2H_x which is produced by ethylene.(136) It appears that the CO insertion step is an essential step for the synthesis of C_{2+} oxygenated compounds. In contrast to Rh catalysts, Pd/SiO_2 is essentially inactive for catalyzing the formation of C_3 oxygenated compounds during addition of ethylene to CO/H_2. Pd is known to be not very active for CO dissociation. There should be an abundance of nondissociatively adsorbed CO for insertion into adsorbed C_2H_x during the addition of ethylene to CO/H_2. Thus, the inability of Pd/SiO_2 to catalyze the formation of C_3 oxygenated from ethylene must be attributed to either its poor CO insertion capability or its very high hydrogenation ability. This suggests that not only the concentration of nondissociatively adsorbed CO but also the relative capability for CO insertion is an important factor for the formation of C_{2+} oxygenated compounds.

It is interesting to note that Rh black is able to produce a significant amount of oxygenated compounds. In contrast, several previous studies on Rh single crystal(123,124) have shown that clean elemental Rh produce only hydrocarbons while preoxidation of Rh metallic crystal results in the formation of oxygenated compounds during Co hydrogenation. Several factors may contribute to the difference in product selectivity between Rh black and Rh metallic single crystal. These include different crystalline surfaces and possible contamination of impurities. Rh black (from Alfa) used for this study consists of 600 ppm of Co and 50 ppm of silica. It is not clear how this trace amount of impurities affect the active sites for product formation.

It has been proposed that Rh cations are responsible for the formation of oxygenated products.(29) Thus, methanol would be formed by direct hydrogenation of CO coordinated to Rh^+ while C_2 oxygenated compounds would be formed by the insertion of CO into CH_x on Rh^+. If direct hydrogenation of CO to methanol and CO insertion are assumed to occur on the same active sites, the selectivity to either methanol or C_2 oxygenates should be dependent on the surface concentration of CH_x for CO insertion and the surface concentration of adsorbed H for hydrogenation. However, there is some evidence against this proposal. Results for Rh/MgO (Table 9-2) show that there is a significant different dependence of the formation of C_2 oxygenates and methanol on the reduction temperatures. For Rh/MgO it would appear that the active sites for CO insertion into adsorbed C_yH_x are different from those for methanol formation.

Addition of ethylene to CO/H_2 over Rh black, Rh/La_2O_3, and Rh/MgO (reduced at 250°C), which are active for both methanol synthesis and C_2 oxygenate synthesis, resulted in a decrease in methanol formation over Rh/MgO (reduced at 250°C) but in essentially no effect on methanol formation over Rh black and Rh/La_2O_3. This is an indication that either mechanisms or active sites are responsible for methanol synthesis over Rh/MgO (reduced at 250°C) are different as opposed to methanol synthesis over Rh black and Rh/La_2O_3. This suppression of methanol formation during ethylene addition has also been observed for Pd/SiO_2. This suggests that the active sites for methanol formation on Rh/MgO (reduced at 250°C) may have certain characteristics similar to those on Pd/SiO_2. Similar suppression of methanol formation during the addition of an olefin (1-hexene) to CO/H_2 over a Cu/ZnO catalyst has been reported by Vedage and Klier.(147) Ponec and coworkers(80,138) have suggested that Pd^{n+} is an active site for methanol synthesis and plays a role similar to that of Cu^+ in the Cu/ZnO catalyst for methanol synthesis. Poels(62) found that Rh/MgO reduced at 215°C, which was active for methanol synthesis, exhibited an ESR signal for Rh^{+2}. He suggested that the presence of unreduced positive ions is an important factor in the production of oxygenated products.

It has been suggested that adsorption of hydrocarbons, especially olefins, on metals may be associated with a transfer of electrons from hydrocarbons to the metal.(141) If this is the case for the added ethylene, the added ethylene will be preferentially adsorbed on metal ion sites such as Pd^{n+}, Rh^{n+}, or Cu^+ to block methanol formation.

The suppression of methanol formation was not observed for Rh/La_2O_3 which is also active for methanol synthesis. This could be due to different active sites or precursors involved in methanol synthesis over these Rh catalysts, Rh/MgO (reduced at 250°C) and Rh/La_2O_3. It has been reported that La_2O_3 itself can participate in the methanol synthesis.(75) Kuznetzov et al.(75) have suggested, based on their NMR results, that CHO and CHO_2 may be formed on La_2O_3 and then hydrogenated to methanol on Rh.

The distinct characteristics of the active sites for methanol synthesis over Rh/La_2O_3 can also be discerned from results of ethanol addition. Addition of ethanol to CO/H_2 over Rh/La_2O_3 resulted in a decrease in methanol formation but this decrease was not observed for other catalysts such as Rh black and Pd/SiO_2.

The results of ethanol addition appear to be complex. The added ethanol is known to be able to react on both metal and oxide surfaces. It has been suggested that adsorbed ethanol exists as ethoxy on metal surfaces.(117) Ethanol can undergo dehydrogenation to acetaldehyde, conversion to methane and C_2 hydrocarbons, and incorporation into higher oxygenated and hydrocarbon products. It can also be dehydrogenated to acetaldehyde on basic sites of an oxide support and be dehydrated to C_2 hydrocarbons on acidic sites of an oxide support. Since dehydration and dehydrogenation involve acidic and basic sites, the acidity/basicity of catalysts may be determined by their dehydration/dehydrogenation selectivities. Comparing the selectivities of CO hydrogenation (Table 9-2) with selectivities of reactions resulting from added ethanol (Table 9-4), it appears that there is no apparent correlation of direct CO hydrogenation selectivity with the acidity/basicity of the catalysts.

Rh/SiO_2 and Rh/MgO (reduced at 400°C) which were active for the synthesis of C_{2+} oxygenates during CO hydrogenation showed a high selectivity for the incorporation of ethanol into C_3 oxygenates during the addition of ethanol to CO/H_2. However, this incorporation was not observed for Rh black which was also active for the synthesis of C_2 oxygenates. This suggests that this incorporation may require the participation of the support either by furnishing active sites or in modifying the properties of Rh.

Pd/SiO_2 exhibited mainly dehydrogenation activity for the added ethanol suggesting that the ethoxy intermediates may be stablized on Pd surfaces may then undergo dehydration to acetaldehyde. Pd/SiO_2 (which is able to form Pd-ethoxy intermediates) may also be able to coordinate methoxy (suggested as methanol precursors)(7,81) leading to high selectivity for methanol formation. In contrast, Rh black, Rh/SiO_2, Rh/La_2O_3, and Rh/MgO which are active not only for oxygenate synthesis but also for hydrocarbon synthesis exhibited relatively high selectivities for the conversion of ethanol to methane and C_2 hydrocarbons. This suggests that part of the ethoxy intermediates produced during CO hydrogenation may undergo secondary reactions leading to the production of hydrocarbons.

Although variously supported Rh catalysts, Rh black, and Pd/SiO_2 are active for methanol synthesis, different mechanisms for methanol formation may be followed on the different catalysts. It is therefore extremely difficult to propose a single mechanism to explain methanol synthesis on these various catalysts. In spite of this complexity, on the basis of the above discussion, it appears there are some correlations of the selectivities of CO hydrogenation with the selectivities of these probe molecule reactions as shown in Table 9-5 and 9-6.

9.4 Conclusions

In addition to the well known difference in CO dissociation activity among these catalysts, one of the major differences between Pd/SiO_2 and Rh based catalysts is the CO insertion capability. Poor CO insertion capability of Pd/SiO_2 leads to the poor activity for catalyzing C_{2+} oxygenate formation during CO hydrogenation.

It appears that the active sites for methanol formation are different from those for C_2 oxygenate formation. Different mechanisms for methanol synthesis may occur on different supported metal catalysts.

Table 9-5 Some Correlations between CO Hydrogenation Selectivity and Product Selectivity from Ethylene Reaction During CO Hydrogenation

$CO + H_2$		$C_2H_4 + CO + H_2$
Synthesis of $C_{2+}OX$	***	Ability to insert CO in absorbed C_2H_4
Lack of ability to Synthesis MeOH	**	Ability to form C_{3+} HC from C_2H_4
Moderate-Strong Selec. + Moderate-Poor Selec. for HC Synthesis	*	Effect of C_2H_4 Addition on r_{MeOH}

*** Strong Correlation
** Moderation Correlation
* Weak Correlation
0 No Apparent Correlation

Table 9-6 Some Correlation between CO Hydrogenation Selectivity and Product Selectivity from Ethanol Reaction During CO Hydrogenation

$CO + H_2$		$EtOH + CO + H_2$
Lack of ability to Syn. MeOH	***	Incorp. of EtOH into $C_{3+}OX$
Lack of ability to syn. MeOH	**	Dehydroxymethylation/ decarbonylation of EtOH (Exception: Rh/La_2O_3)
Synthesis of Hydrocarbons	**	Conversion of EtOH to CH_4, C_2 hydrocarbons
	0	Incorp. of EtOH into C_{3+} hydrocarbons
	0	Effect of EtOH addition on r_{MeOH}

*** Strong Correlation
** Moderation Correlation
* Weak Correlation
0 No Apparent Correlation

10.0 FINAL DISCUSSION

This study was aimed at establishing a better understanding of the effects of alkali promoters and supports on the synthesis of oxygenated compounds, especially of higher alcohols and aldehydes over rhodium catalysts. A probe molecule technique has been developed to investigate the reaction pathways for oxygenate formation and the effects of promotion and of supports on the catalytic properties of rhodium catalysts. This technique has been demonstrated to be an effective way to (a) identify possible reaction networks occurring on these catalysts, (b) study interrelationships between oxygenate and hydrocarbon synthesis, (c) determine the chemical properties of the catalyst surfaces, and (d) investigate the effect of supports and of alkali promotion on the reaction pathways to oxygenates and hydrocarbons. Chapter 3 reports results of an investigation on the reaction pathways to oxygenated compounds and hydrocarbons. The effects of alkali promoters and supports on oxygenate synthesis have been treated in detail in chapters 4-9. In this chapter, the relevant results of all these investigations will be brought together.

10.1 Reaction Mechanisms

Reaction pathways for the formation of oxygenated compounds and hydrocarbons from synthesis gas as shown in Figure 10-1 were proposed on the basis of results reported in Chapter 3 as well as of suggestions reported in the literature. Group VIII metals, such as

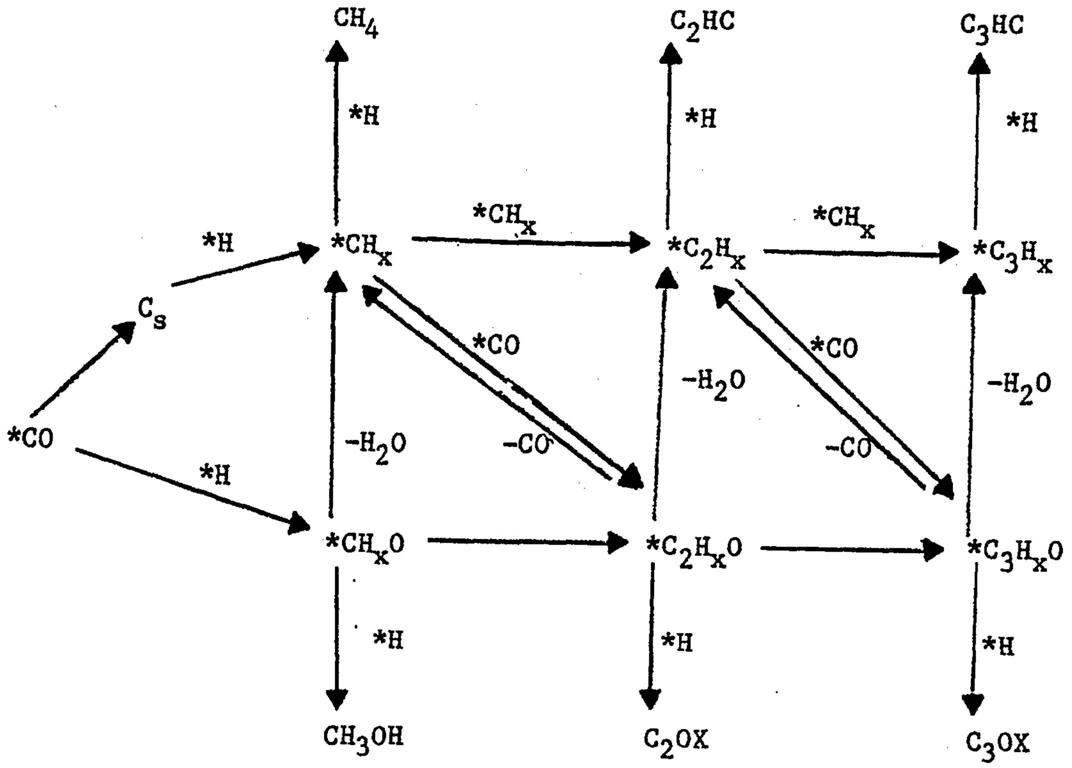

Figure 10-1 Possible Reaction Network for CO Hydrogenation

Ni, Ru, Rh, and Pd, exhibit not only different CO dissociation activities(21) but also variations in catalytic ability for hydrogenation, dehydrogenation, CO insertion, CH_x insertion, dehydration, and hydrogenolysis. These differences in catalytic ability for specific reaction steps lead to different product distributions during CO hydrogenation. Thus, Ni/SiO_2, 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/SiO_2 appear to be unfavorable for the formation of significant amounts of higher hydrocarbons and oxygenated compounds. The most probable reaction pathway to methane from synthesis gas over Ni/SiO_2 is hydrogenation of dissociated CO. Ru/SiO_2, a good higher hydrocarbon synthesis catalyst, demonstrated in the presence of CO and H_2 strong catalytic activity for ethylene hydrogenation, dehydroxymethylation of ethanol, decarbonylation of acetaldehyde, and incorporation of ethanol and acetaldehyde into higher hydrocarbons but weak catalytic activity for hydrogenolysis of ethylene and CO insertion. A poor CO insertion capability and a strong decarbonylation activity prevent the formation of C_{2+} oxygenated compounds, and they exclude oxygenates as major intermediates for hydrocarbon chain growth over Ru/SiO_2. The insertion of CH_x into C_yH_x appears to be a major route for the formation of higher hydrocarbons over Ru/SiO_2.

Rh/SiO_2, a good C_2 oxygenate synthesis catalyst, exhibited strong catalytic activity for the incorporation of ethylene and ethanol into C_3 oxygenated compounds but poor catalytic activity for decarbonylation of acetaldehyde and hydrogenolysis of ethylene in the presence of CO. A strong capability in the incorporation of ethylene and ethanol into C_{3+} oxygenated compounds indicate that both oxygenated and hydrocarbon intermediates could be important for oxygenate chain growth. Both the activity of the catalyst to catalyze CO insertion and the surface concentration of non-dissociatively adsorbed CO are crucial factors for C_2 oxygenate formation. Pd/SiO_2, a methanol synthesis catalyst, showed strong catalytic activity for hydrogenation and poor catalytic activity for CO insertion, dehydroxymethylation of ethanol, and the incorporation of ethylene and ethanol into higher hydrocarbons and oxygenated compounds. The activity in catalyzing probe molecule reactions exhibited by Pd/SiO_2 is somewhat similar to those displayed by Ni/SiO_2, both do not favor the formation of C_{2+} species. Methanol is probably formed directly by hydrogenation of non-dissociated CO; this reaction step has been shown to occur by a study using isotopic tracers.(22)

Table 10-1 summarizes the proposed active sites for these specific reaction steps. It is generally agreed that CO dissociation, hydrogenation, and CH_x insertion take place on metal sites. However, much controversy exists concerning the active sites for CO

Table 10-1 Nature of Active Sites for Specific Reaction Steps

Specific Reactions	Oxidation State	Geometric Requirements
$CO \rightarrow C + O$	metal	ensemble(17,35,36)
$C + XH \rightarrow CH_x$	metal	a small number of(17,35) metal surface atoms
$CH_x + CH_x \rightarrow C_2H_y$	metal	ensemble(36)
$CH_x + CO \rightarrow C_2OX$	metal,(6) metal ion(11,131)	a single atom(11)
$CO + H_2 \rightarrow CH_3OH$	metal(81,144) metal ion(29,62)	

insertion. While there is no definite evidence to support Rh^+ as an active site for CO insertion, there are a number of arguments which favor this proposition.

1. Addition of ethylene to the CO/H_2 reaction mixture results in the formation of propionaldehyde and 1-propanol on Rh catalysts. These reaction steps appear to resemble the hydroformylation reaction. The selectivity for C_2 oxygenates during CO hydrogenation parallels that for C_3 oxygenates during addition of ethylene to CO/H_2. This is an indication that the mechanism for C_2 oxygenate formation by insertion of CO into CH_x may be similar to that for C_3 oxygenate formation by insertion of CO into C_2H_x. Based on the analogy with homogeneous hydroformylation, CO insertion would occur on a $Rh^{\delta+}$ site.

2. The positive charge on Rh^+ results in a decrease in electron back donating capability to break the C-O bond. Therefore, the CO molecule may be preserved for CO insertion.

3. Rh^+ ions may associate with anions such as hydroxyl groups leading to a decrease in hydrogenation activity. Thus, CO insertion into adsorbed CH_x may compete with hydrogenation of CH_x due to this decrease.

If Rh ions are active sites for CO insertion, they may not necessarily have to be stabilized by either alkali promoters or by supports as indicated by the fact that Rh black is active for catalyzing CO insertion (chapter 4). Rh black used for this study consists of 600 ppm of Co and 50 ppm of silica. It is not clear how these impurities affect the active sites for CO insertion. Though Rh oxide is relatively easy to reduce compared with some Group VIII metals such as Ni, Rh^+ ions may exist in an atmosphere of CO. A recent study by Vis(110) has suggested that Rh metal can be oxidized by a dissociatively adsorbed CO.

$$CO + 3Rh \rightarrow RhC + 2Rh^+ + O^{2-} \qquad 10\text{-}1$$

$$2Rh^+ + 4CO \rightarrow 2Rh^+(CO)_2 \qquad 10\text{-}2$$

He has also suggested that Rh^+ may be re-reduced to the metal as follows:

$$O^{2-} + 2Rh^+ + 2CO \rightarrow 2Rh + CO_2 + CO \qquad 10\text{-}3$$

The possibility of this oxidation-reduction process under synthesis conditions may help explain why Rh^+ was not observed for Rh/TiO_2 by Katzer et al.(6) in an ESCA study. Besides the possibility of the formation of the metal ion by oxidation, the protruding atom of a stepped surface has been suggested to have a positive charge.(139) It is possible that oxygen ions of the supports may associate with Rh^+ to stabilize it.(131) Furthermore, different supports undoubtedly exert different effects on Rh ions.

10.2 Effect of Supports

Supports were found to have a great effect not only on the specific reaction steps such as CO dissociation, CO insertion and hydrogenation but also on the secondary reactions of primary products. 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. This selectivity does not correlate with the acidity/basicity of the support. It appears that these results can not be simply explained by the electron donating or withdrawing capabilities of the support. Factors such as effect of support on the reducibility, electronic properties, and morphology of the metal and participation of the support as an active site may complicate the overall observed effect of the support.

Although these effects are very complex, it is instructive to review our results and some propositions and observations in the literature in order to gain an insight into the effect of metal-support interactions on the catalytic properties of Rh metal.

The state of Rh metal on MgO has been found to be strongly dependent on the reduction temperature.(62) Rh/MgO reduced at 215°C which yields a strong Rh^{2+} signal in ESR is active for methanol synthesis while reduction at 314°C results in high selectivity to ethanol.(62) A similar dependence of product distribution over Rh/MgO on reduction temperature has also been reported in Chapter 9. In contrast to Rh/MgO, this dependence of product distribution on reduction temperature has not been observed for Rh/TiO_2.(14) A temperature programmed reduction study on supported Rh catalysts(110) has revealed that supports affect the reducibility of Rh metal. Recently, Kawai et al.(131) have reported that Rh on various oxides (SiO_2, ZnO, and ZrO_2) or TiO_2 on SiO_2 exists in a state between Rh metal and Rh^+. These observations have led us to consider the effects of supports on the reducibility of metal as an important factor of metal-support interactions.

Support effects on the morphology of metal catalysts are well demonstrated by a recent study of supported Pd catalysts by Hicks and Bell.(81) They observed that the crystallite morphology of Pd/SiO_2, which consists of 90% of Pd (100) planes, is independent of Pd weight loading while the crystallite morphology of Pd/La_2O_3 changes with Pd loading. It is possible that the crystallite morphology of Rh metal is also subject to modification by the support. Another aspect of the support effect on the surface of a metal is the migration of La species(143) from La_2O_3 or reduced support material from SMSI supports such as TiO_2(150) onto the surface of the metal particle. This geometric modification of the metal surface by the support could have a great effect on a structure sensitive reaction step.

In addition to direct effects of supports on metals, the supports may also serve as active sites for certain specific reactions. 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 may be precursors for the formation of methanol. On Rh/La_2O_3, these precursors could be formed on La_2O_3 and then be hydrogenated to methanol on the Rh.

Depending on the nature of the support, one specific effect of the support may overwhelm another. It is, therefore, extremely difficult to correlate the catalytic properties of supported metals with a single property of support such as acidity, basicity, Fermi level, and heat of formation of the oxide, etc. The current knowledge of metal-support interactions is still not adequate to resolve these complex effects. This deserves further investigation.

10.3 Effect of Alkali Promoters on Supported Rh Catalysts

Due to the complexity of the combined effects of alkali promoters and supports, it is important to consider first the alkali promotion on Rh black. In chapter 7, we reported that the addition of Li promoters to Rh black results in (a) suppression of hydrogenation, (b) suppression of dehydration, (c) enhancement of the selectivity for CO insertion, and (d) an increase in the activity for CO conversion and C_2 oxygenate formation. Other effects of alkali promotion on the catalytic properties of Rh, such as promotion of CO dissociation, has also been reported in the literature.

The effects of additives such as alkali promoters on metal catalysts can generally be classified into one of two categories: (a) modification of the catalytic properties of the metal as a result of the chemical nature of the additive and (b) blockage of surface sites by the physical presence of the additive. Physical blockage of the surface active sites by alkali promoters would have a great effect on those specific reaction steps which require large ensembles of surface atoms, such as CO dissociation, and would only slightly affect those steps such as hydrogenation, which do not require such large ensembles. Thus, the physical blockage of surface atoms could lead to an enhancement in the selectivities for those products which form on small ensembles of surface atoms. However, alkali promoters are known to be able to enhance adsorption energy and dissociation probability of CO and to suppress hydrogenation of surface carbon and olefins. This seems to suggest that the chemical effect of alkali promoters on CO hydrogenation is more significant than just that due to physical blockage.

There have been several propositions in the recent literature for explaining the mechanisms of alkali promotion. It is important to reexamine these propositions in order to help draw some conclusions. The proposed mechanisms of alkali promotion can be summarized as follows:

- A modification of the electronic properties of the metal.

  Alkali promoters are considered as "electron" donors. The addition of an alkali promoter to a metal results in an increase in electron density of the metal. This mechanism is supported by the observed shift in binding energy of the metal electron on alkali metal-promoted catalysts(44-45) or on alkali metal ion-promoted catalysts.(43,63)

- Participation as an active site.

  Alkali metal ions may provide sites where CO may be C bonded to the transition metal and O-bonded to the alkali metal ions to facilitate CO dissociation.(139) This postulation is based on the analogy between the chemistry of molecular carbonyl complexes and that of chemisorption complexes.

- Stabilization of active sites.

  Alkali promoters may be able to stabilize metal ions against reduction.(62)

- Stabilization of reactive intermediates.

  Alkali metal ions may be able to stabilize the coordinatively unsaturated intermediate to promote CO insertion.(149) This postulation is on the basis of analogy with organometallic chemistry.

It has been noted in a recent paper(139) that in homogeneous solutions reactants and catalysts are free to diffuse to achieve an appropriate configuration for alkali promotion while it may be difficult to form such a configuration for alkali promotion of a heterogeneous surface. Caution has to be taken to apply this type of analogy to explain the alkali promotion of heterogeneous catalysis.

On the basis of our results, we are not able to exclude any of these propositions. But these results of alkali promotion of Rh black may be rationalized by combinations of these propositions. Suppression of hydrogenation brought about by alkali promoters has been explained by an increase in electron density of the metal caused by donation from alkali species.(40-41) This suggestion is based on the assumption that adsorbed hydrogen tends to donate electrons to the metal. If the transfer of electronic charge from the promoter to the metal does occur, this could result in an effective decrease in average oxidation state of the metal causing (a) a decrease in rate of CO insertion (assuming Rh^+ is an active site) and (b) an increase in CO dissociation (increased electron donating ability of metal surface). The observed suppression of hydrogenation may suggest that the electron-donating property of alkali promoters play an important role in alkali promotion. Thus, alkali promoters could hinder the CO insertion resulting in a decrease in activity for C_2 oxygenate formation. In contrast, an enhancement of C_2 oxygenate activity and CO insertion selectivity was observed for Li-promoted Rh black. This may suggest that other effects of alkali promoters such as stabilization of active sites and/or reactive intermediates for C_2 oxygenate formation overwhelm those of alkali promoters in decreasing the oxidation state of the metal surface on these catalysts.

As stated earlier, the protruding atom on a stepped surface has been suggested to have a positive charge.(139) Thus, it is possible that Rh^+ is located on such a stepped surface. Alkali promoters may be in the vicinity of Rh ion to stabilize it against reduction and to stabilize the coordinated intermediate to C_{2+} oxygented compounds.

The effect of alkali promoters on C_{2+} hydrocarbon and C_2 oxygenate selectivities over Rh black and supported Rh catalysts are summarized in Table 10-2. The differences in the effect of alkali

Table 10-2 Effect of Alkali Promoters and Supports on C_2 Oxygenate and C_{2+} Hydrocarbon Selectivities*

		Li	K	Cs
Rh black	C_2OX	+		
	$C_{2+}HC$	−		
TiO_2	C_2OX	0	+	+
	$C_{2+}HC$	0	−	+
La_2O_3	C_2OX	+	−	−
	$C_{2+}HC$	+	+	+
MgO	C_2OX	+	−	+
	$C_{2+}HC$	+	+	−
SiO_2	C_2OX	−	−	−
	$C_{2+}HC$	+	+	+

\+ an increase in selectivity
− a decrease in selectivity
0 no effect
OX = oxygenated compounds
HC = hydrocarbons

*Compared to the unpromoted catalyst

promotion on product selectivity may reflect differences in the effect of alkali promotion on the specific reaction steps. Promotion of C_{2+} oxygenate selectivity on certain alkali-promoted catalyst suggests that alkali promoters modify the catalyst surface in such a way to stablize active sites and/or intermediates for C_2 oxygenate formation. The decrease in C_2 oxygenate selectivity on certain alkali-promoted catalyst suggests that alkali promoter may situate in such a configuration as to decrease the average oxidation state of Rh ion. It is also possible that alkali species locate mainly on metal surfaces to enhance CO dissociation and to suppress hydrogenation resulting in high selectivity for C_{2+} hydrocarbons.

Since CH_x species are the precursors for the formation of hydrocarbons and C_{2+} oxygenated compounds, the suppression of hydrogenation could decrease the rate of CH_x formation resulting in a decrease in overall yields. The decrease in overall yields have been observed for all of alkali-promoted Rh catalysts except in the cases of Li-promoted Rh black and Rh/La_2O_3. This suggests that suppression of hydrogenation did not play an important role during CO hydrogenation over these two catalysts.

It appears that complex factors are involved in alkali promotion of supported Rh catalysts. Factors, such as the distribution and geometric location of alkali promoters on the metal surface could have a great effect on the type of alkali promotion (i.e., a modification of the electronic properties of the metal, participation as an active site, stabilization of active sites, and stabilization of reactive intermediates). This deserves further investigation.

Investigation of alkali promotion on methanol synthesis was limited to that of K-promotion of Pd/SiO_2. The results of this study suggest that the active sites for methanol formation are different from those for methane formation. The major effect of K promotion was identified to be suppression of hydrogenation resulting in a decrease in activity for methanol synthesis. It appears that suppression of hydrogenation is a common effect of alkali promotion on CO hydrogenation.

10.4 Concluding Remarks

This investigation has demonstrated that the addition of probe molecules to the reactant stream not only provides a way to elucidate reaction pathways for oxygenate and hydrocarbon syntheses but also furnishes a way to probe modifications, as a result of alkali promotion, in a number of specific reaction steps occurring during CO hydrogenation.

This study has also shown the network characteristics of hydrocarbon and oxygenate syntheses. A selective C_2 oxygenate synthesis catalyst must have a strong CO insertion activity. However, it seems to be inevitable that hydrocarbons are produced during C_2 oxygenate synthesis. This is evidently due to the fact that C_{2+} oxygenated compounds and hydrocarbons share common intermediates.

APPENDIX A

COMPUTER PROGRAM FOR REACTOR CONTROL

```
10  REM  FLOW SET POINT
100  INPUT "SAMPLING INTERVAL ";TS
110  INPUT "PROPORTIONAL GAIN ";G
120  INPUT "PERIOD ";TAU
130  INPUT "INTEGER TIME ";TI
200  INPUT "HE FLOW 0  ";U0
220  INPUT "H2 FLOW 0  ";G0
230  INPUT "CO FLOW 0  ";B0
240  INPUT "INITIAL TEMP  ";SI
250  INPUT "RATE OF TEMP  ";R
260  INPUT "PERIOD OF RAMP ";PP
270  INPUT "PRESS ";R0
310  INPUT "HE FLOW 1  ";U1
320  INPUT "H2 FLOW 1  ";G1
330  INPUT "CO FLOW 1  ";B1
340  INPUT "TEMP 1  ";S1
345  INPUT "PRESS 1 ";R1
350  INPUT "PERIOD 1  ";P1
410  INPUT "HE FLOW 2  ";U2
420  INPUT "H2 FLOW 2  ";G2
430  INPUT "CO FLOW 2  ";B2
440  INPUT "TEMP 2  ";S2
445  INPUT "PRESS 2 ";R2
450  INPUT "PERIOD 2  ";P2
510  INPUT "HE FLOW 3  ";U3
520  INPUT "H2 FLOW 3  ";G3
530  INPUT "CO FLOW 3  ";B3
540  INPUT "TEMP 3  ";S3
545  INPUT "PRESS 3 ";R3
550  INPUT "PERIOD 3  ";P3
610  INPUT "HE FLOW 4  ";U4
620  INPUT "H2 FLOW 4  ";G4
630  INPUT "CO FLOW 4  ";B4
640  INPUT "TEMP 4  ";S4
645  INPUT "PRESS 4 ";R4
650  INPUT "PERIOD 4  ";P4
700  INPUT "SAMPLING TIME 1 ";K1
701  INPUT "SAMPLING TIME 2 ";K2
702  INPUT "SAMPLING TIME 3 ";K3
703  INPUT "SAMPLING TIME 4 ";K4
704  INPUT "SAMPLING TIME 5 ";K5
705  INPUT "SAMPLING TIME 6 ";K6
706  INPUT "SAMPLING TIME 7 ";K7
708  INPUT "SAMPLING TIME 8 ";K8
```

```
880  & TIME TO HR,MN,SC
881  & DAY TO YR,MO,DT,DA
890 P0 = (DT * 24 + HR) * 60 + MN + (SC / 60)
900 V1 = 0
910 E1 = 0
915 N = 1
920  & TIME TO HR,MN,SC
921  & DAY TO YR,MO,DT,DA
925 P = (DT * 24 + HR) * 60 + MN + (SC / 60)
927 PA = P - P0
928 KA =  INT (PA)
930  IF PA > P3 GOTO 980
931  IF PA > P2 GOTO 970
932  IF PA > P1 GOTO 960
933  IF PA > PP GOTO 954
935 S = PA * R + SI
939 RS = R0
940 ES = U0
945 HS = G0
950 CS = B0
951  GOTO 990
954 RS = R1
955 S = S1
956 ES = U1
957 HS = G1
958 CS = B1
959  GOTO 990
960 S = S2
961 ES = U2
962 HS = G2
963 CS = B2
964 RS = R2
969  GOTO 990
970 S = S3
971 ES = U3
972 HS = G3
973 CS = B3
974 RS = R3
979  GOTO 990
980 S = S4
981 ES = U4
982 HS = G4
983 CS = B4
984 RS = R4
990  IF K1 = KA GOTO 1005
991  IF K2 = KA GOTO 1008
992  IF K3 = KA GOTO 1011
993  IF K4 = KA GOTO 1014
994  IF K5 = KA GOTO 1017
995  IF K6 = KA GOTO 1020
```

```
996  IF K7 = KA GOTO 1023
997  IF K8 = KA GOTO 1026
998  GOTO 1050
1005 W1 = M
1006 X1 = PR
1007  GOTO 1040
1008 W2 = M
1009 X2 = PR
1010  GOTO 1040
1011 W3 = M
1012 X3 = PR
1013  GOTO 1040
1014 W4 = M
1015 X4 = PR
1016  GOTO 1040
1017 W5 = M
1018 X5 = PR
1019  GOTO 1040
1020 W6 = M
1021 X6 = PR
1022  GOTO 1040
1023 W7 = M
1024 X7 = PR
1025  GOTO 1040
1026 W8 = M
1027 X8 = PR
1028  GOTO 1040
1040  & BOUT.(DV) = 30
1042  & PAUSE = .1
```

```
1050  & AIN,(D#) = 0,(TV) = V,(C#) = 5
1052  & WRDEV,(DV) = 1,(W#) = 2,(D#) = 0
1054  & AIN,(D#) = 0,(TV) = VA,(C#) = 4
1060 V = 5 * 1E6 * (V - 2048) / (91.1 * 2048)
1080 VA = 5 * 1E6 * (VA - 2048) / (91.1 * 2048)
1100 M = VA * (2.4383248 * 1E - 2 + VA * (9.7830251 * 1E - 9 + VA * (3.6
    276965 * 1E - 12 + VA * ( - 2.576438 * 1E - 16)))
1120 T = V * (2.4383248 * 1E - 2 + V * (9.7830251 * 1E - 9 + V * (3.6276
    965 * 1E - 12 + V * ( - 2.576438 * 1E - 16)))
```

```
1140 E2 = S - T
1160 V2 = V1 + G * ((E2 - E1) + (TS / TI) * E2)
1180  IF V2 <  = 0 THEN V2 = 0
1200  IF V2 >  = TAU THEN V2 = TAU
1220 F1 = V2
1260  & BOUT,(DV) = 1
1280  & PAUSE = F1
1300 F2 = TAU - V2
1340  & BOUT,(DV) = 0
1360  & PAUSE = F2
1380 V1 = V2
1400 E1 = E2
1420  REM  FLOW CONTROL
1440 EO = (ES / 400 + 5) * 409.6
1460 HO = (HS / 400 + 5) * 409.6
1480 CO = (CS / 400 + 5) * 409.6
1490 RS = (RS / 100 + 5) * 409.6
1500  & AOUT,(DV) = EO,(C#) = 0
1520  & AOUT,(DV) = HO,(C#) = 1
1540  & AOUT,(DV) = CO,(C#) = 2
1545  & AOUT,(DV) = RS,(C#) = 3
1546 M =  INT ((M + 0.05) * 100) / 100
1550 N = N + 1
1555  IF N > 5 GOTO 1600
1560  GOTO 920
1580  REM  PRINT OUT
1600  & AIN,(TV) = IE,(C#) = 0
1620  & AIN,(TV) = IH,(C#) = 1
1640  & AIN,(TV) = IC,(C#) = 2
1650  & AIN,(TV) = PR,(C#) = 6
1660 ER = (IE / 409.6 - 5) * 400
1665 ER =  INT ((ER + 0.05) * 100) / 100
1666  IF ER <  = 0 THEN ER = 0
1680 HR = (IH / 409.6 - 5) * 400
1685 HR =  INT ((HR + 0.05) * 100) / 100
1686  IF HR <  = 0 THEN HR = 0
1700 CR = (IC / 409.6 - 5) * 400
1705 CR =  INT ((CR + 0.05) * 100) / 100
1706  IF CR <  = 0 THEN CR = 0
1710 PR = (PR / 409.6 - 5) * 100
1715 PR =  INT ((PR + 0.05) * 100) / 100
1720  PRINT "HE FLOW RATE  ";ER
1730  PRINT "    "
1740  PRINT "H2 FLOW RATE  ";HR
1750  PRINT "    "
1760  PRINT "CO FLOW RATE  ";CR
1770  PRINT "    "
```

```
1771  PRINT "    "
1775 T =  INT ((T + 0.05) * 100) / 100
1780  PRINT "FURNACE TEMP  ";T
1800  PRINT "REACTOR TEMP  ";M
1900  PRINT "    "
2000  PRINT "REACOTR PRESS ";PR
2005  PRINT "        "
2015 PA =  INT ((PA + 0.05) * 100) / 100
2020  PRINT "REAL TIME ";PA
2025  PRINT "     "
2030  PRINT "    "
2031  PRINT "T1=";W1;" P1=";X1;" T2=";W2;" P2=";X2
2032  PRINT "T3=";W3;" P3=";X3;" T4=";W4;" P4=";X4
2033  PRINT "T5=";W5;" P6=";X6;" T6=";W6;" P6=";X6
2034  PRINT "T7=";W7;" P7=";X7;" T8=";W8;" P8=";X8
2035  PRINT "        "
2040  GOTO 915
```

APPENDIX B

ERROR ANALYSIS FOR RATE MEASUREMENTS

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The rate of formation of a specfic product in a differential reactor can be calculated by the following equation.

$$\gamma = \frac{V.C.\ 60\ \text{min/hr}}{W \cdot \frac{1}{1000}\ \text{kg/g}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (B\text{-}1)$$

where γ = the rate of formation of a specific product, mole/kg hr.

V = volumetric flow rate, cc/min

C = concentration of the specific product in the reactant stream, mole/cc.

= weight of catalysts, g

The error in rate of product formation derived from these three measured quantities is given by

$$E_r = E_\gamma + E_c + E_w \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (B\text{-}2)$$

E_r, E_v, E_c, E_w are the fractional error of γ, V, C, and W, respectively. The Brooks 5850 flow controller used for this study can be measured accurately to ±1 cc/min and the accuracy of a Gram-Atic Balance (Fischer Scientific) is within ± 0.0001 g. The fractional error in concentration caused by calibration and sampling is approximately 5%. For a type run, W is 0.75 g, V is 90 cc/min. The fractional error in measured quantity can be determined to be E_V = 1/90 = 1.1%, E_c = 5%, and E_W = 0.001/0.75 = 0.013%.

Substituting these values, E_V, E_c, and E_W into Equation B-2, E_Y is obtained to be 6.08%.

APPENDIX C

Product Distribution during CO Hydrogenation and Ethylene Reaction, Ethanol Reaction, and Acetaldehyde Reaction during CO Hydrogenation over Ni, Ru, Rh, Pd, and Alkali-Promoted Rh and Pd Catalysts

Table C-1 Activity and Product Distribution during CO Hydrogenation over Rh Black(a) and Li-Rh Black(b)

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300(a)	10	30	1.6	6.8	39.4	6.4	5.1	41.0	1.6	0	0
300(a)	10	250	0.75	15.2	26.1	3.0	11.8	41.5	2.3	0.1	0
298(a)	10	360	0.78	15.1	25.6	5.0	11.3	41.0	1.7	0.3	0
278(a)	10	470	0.71	13.4	28.4	3.5	8.2	43.1	1.2	1.9	0.3
298(a)	10	800	0.73	18.6	30.1	3.6	2.7	42.9	2.1	0	0
300(a)	10	1040	0.48	21.1	41.6	5.0	14.5	15.5	2.3	0	0
300(a)	10	1180	0.51	21.1	38.6	4.0	21.3	10.0	4.3	0.7	0
300(b)	10	30	1.9	30.7	8.8	8.1	17.7	25.8	6.4	2.5	0
300(b)	10	120	1.7	33.2	10.5	7.8	14.6	23.3	6.7	3.9	0

$CO/H_2 = 1$

$$\text{Selectivity to a specific product} = \frac{\text{number of moles of a specific product}}{\text{total number of moles of products}}$$

Table C-2 Activity and Product Distribution during CO Hydrogenation over Rh/TiO_2

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
308	10	60	37.9	56.2	2.6	17.6	0.075	3.2	0.9	1	19.4
305	10	135	37.7	72.5	3.0	12.5	0.1	4.0	1.2	2	0.5
301	10	300	17.3	74.8	3.0	15.3	0.3	4.4	1.1	1	0.1
300	10	420	20.1	75.4	2.8	15.0	0.4	4.4	1.2	1	0.7
300	10	540	17.4	76.1	2.8	13.5	0.3	4.5	1.2	1.0	0.6
285	10	660	13.3	67.1	3.1	11.7	2.5	8.1	2.9	3.3	1.3
275	10	780	7.2	61.6	3.3	11.2	6.2	12.8	3.9	1.0	0

$CO/H_2 = 2$

Table C-3 Activity and Product Disbribution during CO Hydrogenation over Li-Rh/TiO_2

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	15.7	63	3.6	15.7	0.4	4.6	2.3	3.3	7.1
300	10	120	18.0	37.4	2.0	9	0.2	2.7	1.5	1.6	45.6
300	10	210	7.3	70.5	4.0	13.3	0.5	5.0	3.0	2.2	1.5
300	10	300	6.4	71.9	4.2	12.7	0.6	5.0	3.0	1.2	1.4
289	10	480	3.7	68.1	4.4	12.1	0.7	5.5	4.5	1.3	3.4
278	10	660	2.2	59.1	4.3	12.6	1.3	7.7	6.9	2.9	5.2

$CO/H_2 = 2$

Table C-4 Activity and Product Distribution during CO Hydrogenation over K-Rh/TiO_2

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
304	10	30	6.8	68.6	3.9	10.1	0.3	2.8	6.2	6.4	1.7
300	10	120	4.3	68.5	4.5	7.4	0.3	2.0	5.4	6.8	5.1
300	10	210	2.8	70.5	3.9	7.0	0.4	2.2	5.7	6.0	4.3
300	10	300	1.8	65.5	4.1	6.7	0.7	2.8	7.8	7.5	4.9
300	10	500	1.4	70.0	4.1	6.2	1.4	3.2	7.4	7.7	0
310	10	600	2.4	72.1	3.9	5.6	0.9	2.1	4.7	5.4	5.3
320	10	800	3.2	80.5	4.1	5.0	0.5	1.6	3.3	4.8	0.2

$CO/H_2 = 2$

C-5 Activity and Product Distribution during CO Hydrogenation over Cs-Rh/TiO$_2$

T(^{o}C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	C_{4+}OX
300	10	30	0.95	50.5	7.5	22	0.7	0.6	9.1	6.8	2.8
300	10	110	0.70	48.6	15.7	13.6	1.0	0	10.2	6.2	4.7
300	10	210	0.47	49.3	9.7	13.5	2.3	0.6	11.2	7.0	6.4
300	10	310	0.48	42.4	19.8	11.4	2.7	0.9	9.6	7.6	5.6
282	10	420	0.20	41.0	13.7	14.7	7.2	0	13.4	10.0	0
266	10	530	0.13	26.3	29.7	12.2	12.1	0	11.2	8.5	0
251	10	640	0.10	17.6	24.1	15.3	18.6	0	8.8	15.6	0

CO/H$_2$ = 2

Table C-6 Activity and Product Distribution during CO Hydrogenation over Rh/SiO_2

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300(a)	10	30	1.81	50.6	9.0	12.4	0.16	2.2	24.1	1.9	0
300(a)	10	120	1.2	43.8	7.9	6.3	0.4	8.0	26.1	1.2	6.3
300(a)	10	240	1.0	35.7	8.3	5.7	0.6	13.6	27.3	1.3	7.5
300(a)	10	360	1.0	31.4	8.1	5.0	0.6	15.9	27.2	1.7	10.1
300(b)	10	480	0.49	33.8	9.8	5.3	0.9	17.9	26.8	0.9	4.6
300(b)	10	600	0.23	24.7	14.1	5.6	1.4	15.5	24.8	0.3	13.8
300(b)	10	720	0.12	19.0	16.4	6.2	1.8	15.9	21.4	0.3	19.0

(a) $CO/H_2 = 2$ (b) $CO/H_2 = 1$

Table C-7 Activity and Product Distribution during CO Hydrogenation over $Li-Rh/SiO_2$

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	0.73	36.2	12.6	3.3	0.8	8.4	23.0	3.4	12.3
300	10	230	0.63	36.5	11.0	6.8	0.9	7.8	25.9	2.1	9.0
300	10	330	0.64	37.4	7.9	6.4	1.4	8.4	26.3	2.8	9.4
285	10	370	0.43	31.6	7.8	6.6	1.6	8.2	26.3	2.3	15.6
270	10	470	0.16	32.5	10.4	6.4	1.6	8.6	28.4	2.1	10.0
255	10	705	0.07	28.7	15.0	8.9	2.9	12.9	25.5	6.1	0

$CO/H_2 = 1$

Table C-8 Activity and Product Distribution during CO Hydrogenation over K-Rh/SiO_2

$T(^{o}C)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole%)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	0.12	48.3	13.5	6.6	0	6.2	22.8	1.7	0.9
300	10	140	0.08	46.3	14.5	7.4	1	0.1	26.1	3.6	1.0
300	10	250	0.09	41.6	14.2	10.0	0.4	3.2	23.7	6.6	0.3
300	10	360	0.09	39.8	14.6	10.7	0.8	1.1	23.2	9.8	0

$CO/H_2 = 1$

Table C-9 Activity and Product Distribution during CO Hydrogenation over Cs-Rh/SiO_2

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
301	10	30	0.55	17.6	52.5	10.1	1.3	6.0	6.5	5.7	0
301	10	130	0.20	24.2	16.1	10.7	3.0	1.9	9.3	23.1	1.1
300	10	230	0.06	32.4	25.4	19.7	2.9	0	13.2	0	3.0
300	10	330	0.21	33.3	26.3	19.7	3.3	0	13.0	2.7	0.4
288	10	370	0.13	25.9	30.5	22.7	3.0	0	11.5	3.3	3.1
272	10	470	0.11	17.2	39.0	28.4	5.9	0	6.9	2.6	0
258	10	705	0.04	22.3	3.6	50.6	2.4	0	6.2	0	8.2

$CO/H_2 = 1$

Table C-10 Activity and Product Distribution during CO Hydrogenation over Rh/La_2O_3

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}.	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	1.4	33.2	8.7	7.8	23.8	18.8	1.6	4.8	0.5
300	10	130	0.97	36.6	6.1	7.1	22.5	17.8	3.5	3.4	2.8
300	10	230	0.88	40.5	6.6	7.6	19.9	18.5	3.6	4.3	0.2
300	10	330	1.05	42.5	6.7	7.5	20.3	16.9	3.3	3.8	0.2
286	10	430	0.75	32.5	5.1	7.1	28.8	20.0	3.5	3.0	0.1
270	10	530	0.35	22.6	6.7	5.2	43.6	15.8	3.8	1.7	0.1
255	10	630	0.4	14.2	4.7	4.4	58.6	12.2	4.0	1.4	0.2

$CO/H_2 = 1$

Table C-11 Activity and Product Distribution during CO Hydrogenation over Li-Rh/La_2O_3

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
304	10	30	1.6	22.8	24.4	10.1	18.3	19.7	2.0	2.2	0
298	10	130	1.7	21.9	9.5	10.8	18.7	28.8	4.2	4.8	0.9
300	10	230	3.5	22.6	9.7	10.5	18.7	28.6	4.6	7.9	0.2
300	10	330	1.5	22.6	9.3	10.5	18.1	29.6	4.5	7.7	0.2
285	10	430	0.96	18.3	9.8	8.7	26.0	26.9	4.8	4.0	0.1
270	10	530	0.40	13.3	8.4	6.4	37.0	23.4	5.3	5.8	0.1
256	10	630	0.20	10.0	9.1	6.2	50.1	15.4	5.7	3.2	0

$CO/H_2 = 1$

Table C-12 Activity and Product Distribution during CO Hydrogenation over K-Rh/La_2O_3

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
299	10	30	1.2	30.4	25.5	7.5	19.9	12.8	0.6	2.8	0
300	10	130	2.2	35.6	8.1	7.9	24.5	15.9	3.2	4.1	0
300	10	230	3.6	31.8	9.9	8.2	23.3	17.3	3.6	4.6	0
300	10	330	2.9	29.0	10.7	8.1	23.3	18.4	4.4	5.7	0
284	10	430	0.25	22.9	8.8	8.1	33.4	16.7	5.0	4.9	0
269	10	530	0.16	15.2	10.1	7.4	42.1	11.6	5.7	5.2	0
254	10	630	0.18	11.1	10.8	8.3	50.9	9.3	4.9	4.4	0

$CO/H_2 = 1$

Table C-13 Activity and Product Distribution during CO Hydrogenation over Cs-Rh/La_2O_3

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	1.5	36.6	5.7	8.7	39.7	4.7	0	5.4	0
300	10	180	0.9	44.3	10.6	12.4	16.6	2.4	7.4	6.0	0
300	10	250	0.33	41.6	10.1	17.5	8.7	1.9	6.5	13.6	0
300	10	370	0.21	45.6	10.9	13.0	12.9	2.0	8.6	6.8	0
286	10	490	1.7	35.3	11.4	12.6	22.1	4.0	9.5	4.7	0
270	10	610	0.099	24.2	11.3	14.2	27.6	1.6	8.4	11.9	0
258	10	730	0.05	19.4	12.1	11.6	41.7	0.9	7.6	4.5	0

$CO/H_2 = 1$

Table C-14 Activity and Product Distribution during CO Hydrogenation over Rh/MgO

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	5.6	54.4	8.6	14.9	1.8	14	6.2	0.1	0
300	10	140	5.4	51.1	7.4	11.3	0.5	16.8	10.5	1.5	0.9
300	10	250	5.1	52.5	7.1	10.9	0.8	16.6	10.5	0.5	1.1
300	10	360	5.2	55.1	7.3	11.6	0.5	13.3	10.8	0.6	0.8
280	10	470	2.8	48.2	6.4	9.0	0.8	20.6	13.4	0.8	0.8
268	10	580	1.0	29.1	4.7	6.4	2.0	40.1	11.2	4.1	2.4
250	10	690	0.5	19.7	4.5	4.6	2.0	59.7	8.7	0.7	0.1
250*	10	30	0.25	34.8	5.4	5.8	22.4	24.6	5.7	1.3	0

$CO/H_2 = 1$

Table C-15 Activity and Product Distribution during CO Hydrogenation over Li-Rh/MgO

$T(^{o}C)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
305	10	30	9.1	27.9	17.9	30.1	0	7.4	14.4	2.3	0
301	10	140	3.9	27.4	13.5	28.6	2.0	6.7	17.1	1.9	2.8
300	10	250	2.4	27.7	14.5	21.7	3.6	10.5	18.1	2.3	1.6
300	10	360	1.9	25.7	14.1	20.7	3.0	14.2	17.4	3.8	0.8
282	10	470	0.71	19.8	19.0	16.7	6.8	15.4	17.4	2.9	2.0
267	10	580	0.27	15.6	24.5	13.2	5.2	20.4	16.2	4.6	0.3
254	10	690	0.11	12.9	34.0	10.7	11.5	13.2	14.5	2.7	0.5

$CO/H_2 = 1$

Table C-16 Activity and Product Distribution during CO Hydrogenation over K-Rh/MgO

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	0.34	26.9	35.6	11.3	3.3	14.4	5.8	2.2	0.5
300	10	240	0.53	34.6	28.6	18.1	1.9	5.0	9.4	1.1	1.3
300	10	360	0.39	38.4	15.0	18.1	3.4	7.4	10.7	4.0	3.0
282	10	470	0.29	29.3	18.8	14.6	3.2	12.4	10.3	4.2	7.2
254	10	690	0.13	17.4	25.7	6.9	7.4	35.8	5.1	1.7	0

$CO/H_2 = 1$

Table C-17 Activity and Product Distribution during CO Hydrogenation over Cs-Rh/MgO

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
298	10	30	0.25	14.7	38.3	24.1	5.1	6.1	1.0	6.9	3.8
300	10	140	0.12	21.5	25.2	11.8	12.3	20.1	3.1	6.0	0
300	10	250	0.10	23.5	25.3	13.2	12.0	15.7	3.5	6.8	0
300	10	360	0.07	34.1	12.0	15.6	8.5	20.3	4.2	5.3	0
277	10	470	0.04	20.8	6.7	12.3	20.1	28.6	6.2	5.3	0
263	10	580	0.04	11.9	25.2	8.5	14.8	33.8	2.8	3.0	0
249	10	690	0.03	7.1	20.4	6.5	19.9	42.7	1.9	1.5	0

$CO/H_2 = 1$

Table C-18 Activity and Product Distribution over Rh/Al_2O_3

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
320	10	30	25.9	90.8	3.4	5.5	0	0	0.3	0	0
301	10	140	9.7	86.9	2.2	4.6	1.5	3.4	0.9	0.15	0.3
301	10	250	8.9	87.1	2.2	4.6	1.5	3.5	0.9	0.2	0
300	10	360	8.0	88.7	2.1	3.8	1.3	2.6	0.9	0.3	0.3
287	10	470	4.9	81.1	3.1	3.8	2.3	5.8	2.3	0.5	1.1
271	10	580	2.3	77.1	2.0	4.6	4.4	7.7	2.7	0.2	1.3
256	10	690	1.3	62.8	1.9	4.7	9.7	14.6	4	0.5	1.8

$CO/H_2 = 1$

Table C-19 Activity and Product Distribution during CO Hydrogenation over K-Rh/Al_2O_3

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
300	10	30	6.5	83.5	2.1	5.5	1.0	6.5	1.4	0	0
300	10	140	4.2	85.5	2.0	4.4	1.2	3.2	2.8	0.5	0.4
298	10	250	4.5	85.7	2.3	4.3	1.0	2.8	2.9	0.3	0.7
300	10	360	3.8	85.1	2.1	4.2	1.1	3.0	3.2	0.2	0.9
282	10	470	3.0	83.6	1.9	4.7	1.5	5.4	2.4	0.3	0.2
266	10	580	1.4	80.5	2.1	5.1	1.6	7.5	2.4	0.6	0.2

$CO/H_2 = 1$

Table C-20 Activity and Product Distribution during CO Hydrogenation over Cs-Rh/Al_2O_3

T(°C)	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
301	10	30	3.3	83.8	3.1	7.6	0.9	2.9	1.5	0.2	0
300	10	140	2.3	84.0	3.2	6.4	1.2	1.9	2.8	0.3	0.2
300	10	250	2.1	84.5	3.0	5.7	1.3	1.6	3.1	0.5	0.3
300	10	360	1.9	83.6	3.0	8.7	1.3	1.9	3.4	0.7	0.4
283	10	470	0.99	78.6	4.0	6.0	2.1	2.4	5.2	1.1	0.6
266	10	580	0.45	73.5	5.3	7.2	2.7	2.5	7.4	0.8	0.6
252	10	690	0.25	58.8	10.8	7.6	7.1	4.3	9.0	2.0	0.4

$CO/H_2 = 1$

Table C-21 Activity and Product Distribution during CO Hydrogenation over Pd/SiO_2 and $K-Pd/SiO_2$

$T(^oC)$	P (atm)	t (min)	Rate of CO Conv. (mole/kg/hr)	Product Selectivity (mole %)							
				C_1	C_2	C_{3+}	MeOH	EtOH	MeCHO	C_3OX	$C_{4+}OX$
275(a)	10	70	1.5	1.2	1.1	1.4	96.3	0	0	0	0
300(a)	10	110	2.1	1.5	0.8	1.3	95.9	0	0	0.5	0
300(a)	10	360	2.7	0.9	1.4	0.6	97.1	0	0	0	0
274(b)	10	135	0.27	7.9	8.3	6.2	77.5	0	0	0.1	0
301(b)	10	180	0.45	11.1	7.4	4.6	68.2	0.8	2.5	5.4	0
300(b)	10	380	0.53	7.9	20.5	6	60.6	0	2.5	2.5	0
277(c)	10	90	0.22	33.3	27.7	24.2	10.8	0	2.7	1.3	0
300(c)	10	190	0.37	35.0	16.2	16.2	27.8	1.3	3.5	0	0
300(c)	10	360	0.38	22.5	29.9	7.8	36.7	0	3.1	0	0

(a)K/Pd = 0 (b)K/Pd = 0.6 (c)K/Pd = 1.8

Table C-22 Product Selectivity from Ethylene Reaction during CO Hydrogenation over Rh Black, Rh/TiO_2, Ru/SiO_2, Ni/SiO_2, Pd/SiO_2 and Alkali Promoter Catalysts

Catalysts	mole % Ethylene added	Rate of Ethylene Conv. (mole/kg/hr)	Product Selectivity (mole %)			
			CH_4	C_2H_6	C_{3+}	C_3OX
Rh Black	3	6.42	0	76.2	0.3	23.5
Li-Rh Black	3.5	1.72	0	61.5	0.5	38.3
Rh/TiO_2*	2.3	8.3	0	92.7	4.8	2.5
Li-Rh/TiO_2*	2.3	4.07	0	87.2	6.0	6.8
K-Rh/TiO_2*	2.3	1.20	0	85.0	13.5	1.5
Cs-Rh/TiO_2*	2.3	0.19	0	38.4	60.0	1.6
Ru/SiO_2	2.8	8.12	0	97.2	2.0	0.7
Ni/SiO_2	1.1	8.65	5	90	1	3.1
Pd/SiO_2**	3.3	36.2	0	99.5	0.3	0.3
0.6K-Pd/SiO_2	3.5	35.0	0	99.5	0.1	0.4
1.8K-Pd/SiO_2	3.3	5.8	0	96.5	0.5	3.0

$CO/H_2 = 1$, 300°C, 10 atm

*$CO/H_2 = 2$

Table 23 Product Selectivity from Ethylene Reaction during CO Hydrogenation over Rh/Al_2O_3, Rh/SiO_2, and Alkali-Promoted Rh/Al_2O_3 and Rh/SiO_2

Catalysts	mole % Ethylene added	Rate of Ethylene Conv. (mole/kg/hr)	Product Selectivity (mole %)			
			C_{H4}	C_2H_6	C_{3+}	C_3OX
Rh/Al_2O_3	3.0	9.15	0	99.3	0.6	0.1
$K-Rh/Al_2O_3$	3.0	6.9	0	95.6	0.1	4.3
$Cs-Rh/Al_2O_3$	3.0	6.6	0	95.4	0.2	4.4
Rh/SiO_2	3.1	6.4	0	76.2	0.3	23.5
$Li-Rh/SiO_2$	3.1	1.48	0	55.4	0.1	44.5
$K-Rh/SiO_2$	3.1	0.42	0	59.1	0.8	40.1
$Cs-Rh/SiO_2$	3.1	0.31	0	57.5	1	41.5

$CO/H_2 = 1$, 300°C, 10 atm

Table C-24 Product Selectivity from Ethylene Reaction during CO Hydrogenation over Rh/La_2O_3, Rh/MgO, and Alkali-Promoted Rh/La_2O_3 and Rh/MgO

Catalysts	mole % Ethylene added	Rate of Ethylene Conv. (mole/kg/hr)	Product Selectivity (mole %)			
			CH_4	C_2H_6	C_{3+}	C_3OX
Rh/La_2O_3	2.6	2.53	0	85.8	0.3	13.9
$Li-Rh/La_2O_3$	2.6	2.64	0	83.7	0.3	15.9
$K-Rh/La_2O_3$	2.6	1.23	0	82.8	5.6	11.6
$Cs-Rh/La_2O_3$	2.6	0.21	0	56.9	16.7	26.3
Rh/MgO	3.1	5.37	0	87.6	2.4	9.9
Li-Rh/MgO	3.0	4.55	0	88	0	12
K-Rh/MgO	3.0	0.72	0	80.5	0.4	19.1
Cs-Rh/MgO	3.0	0.119	0	84	0	16

$CO/H_2 = 1$, 300°C, and 10 atm

Table C-25 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Rh, Ni, Ru, and Pd Catalysts

Catalysts	mole % EtOH added	Rate of EtOH Conv. (mole/kg/hr)	Product Selectivity (mole %)							
			CH_4	C_2	C_{3+}	MeOH	MeCHO	C_3OX	EtOAc	Butyraldehyde
Rh Black	0.9	0.12	0	8.7	0	0	91.3	0	0	0
Li-Rh Black	1.3	0.13	22	0	0	0	64.3	10.8	2.7	0
Rh/MgO	0.45	0.095	27.2	0	0	0	52.4	20	0.4	0
Ni/SiO_2	0.75	0.16	0	0	1.8	0	91	3.7	0	3.1
Ru/SiO_2	2.5	6.5	74.6	10	13.2	0.5	1.4	0	0.2	0
Pd/SiO_2	0.85	0.54	0.7	4.2	3.3	0	87.6	2.6	0	2

Table C-26 Product Selectivity from Ethanol Reaction during CO Hydrogenation over Rh/Al_2O_3, Rh/SiO_2, Rh/La_2O_3, La_2O_3 and Alkali Promoted Catalysts

Catalysts	mole % EtOH added	Rate of EtOH Conv. (mole/kg/hr)	Product Selectivity (mole %)						
			CH_4	C_2	C_{3+}	MeOH	MeCHO	C_3OX	EtOAc
Rh/Al_2O_3	0.3	0.118	0	16.9	16.9	0	35.5	3.3	27.1
$K-Rh/Al_2O_3$	0.6	0	0	0	0	0	0	0	0
$Cs-Rh/Al_2O_3$	0.1	0	0	0	0	0	0	0	0
Rh/SiO_2	0.65	0.28	15.1	2.1	3.0	6	20.8	38.6	14
$Li-Rh/SiO_2$	0.45	0.41	20	8.6	4.6	6	14	38.5	8.3
$K-Rh/SiO_2$	0.48	0.26	53.2	2.6	3.8	0	21.6	1	17.8
Rh/La_2O_3	0.11	0.27	84	6	9	0	0.5	0	0
$Li-Rh/La_2O_3$	0.28	0.15	58	19.4	3.6	0	19	0	0
$K-Rh/La_2O_3$	0.47	0.038	0	0	0	0	100	0	0
$Cs-Rh/La_2O_3$	0.68	0.002	0	0	0	0	100	0	0
La_2O_3	0.99	0.028	0	0	0	0	100	0	0

$CO/H_2 = 1$, 300°C, 10 atm

Table C-27 Product Selectivity from Acetaldehyde Reaction during CO Hydrogenation over Rh, Ni, And Ru Catalysts

Catalysts	mole % MeCHO added	Rate of MECHO Conv. (mole/kg/hr)	Product Selectivity (mole %)					
			CH_4	C_2	C_{3+}	EtOH	C_3OX	C_4OX
Rh Black	2.2	17.5	0.8	63.4	0	12.9	2.2	0.3
Li-Rh Black	3.4	7.8	0.4	49.4	0	47.2	2.3	0
Rh/Al_2O_3	0.5	1.3	0	50.1	8.8	33.2	0.92	6.8
Rh/SiO_2	0.73	1.5	4.8	0.3	3.2	8.7	2.3	1.2
Rh/MgO	2.2	2.2	2.2	0	72.6	18.8	0	0
Ni/SiO_2	0.87	4.4	13	1.1	4.3	68	1.8	10.4
Ru/SiO_2	2.4	6.7	60.7	10.0	9.6	19.1	0.46	0.1

CO/H_2 = 1, 300°C, 10 atm

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