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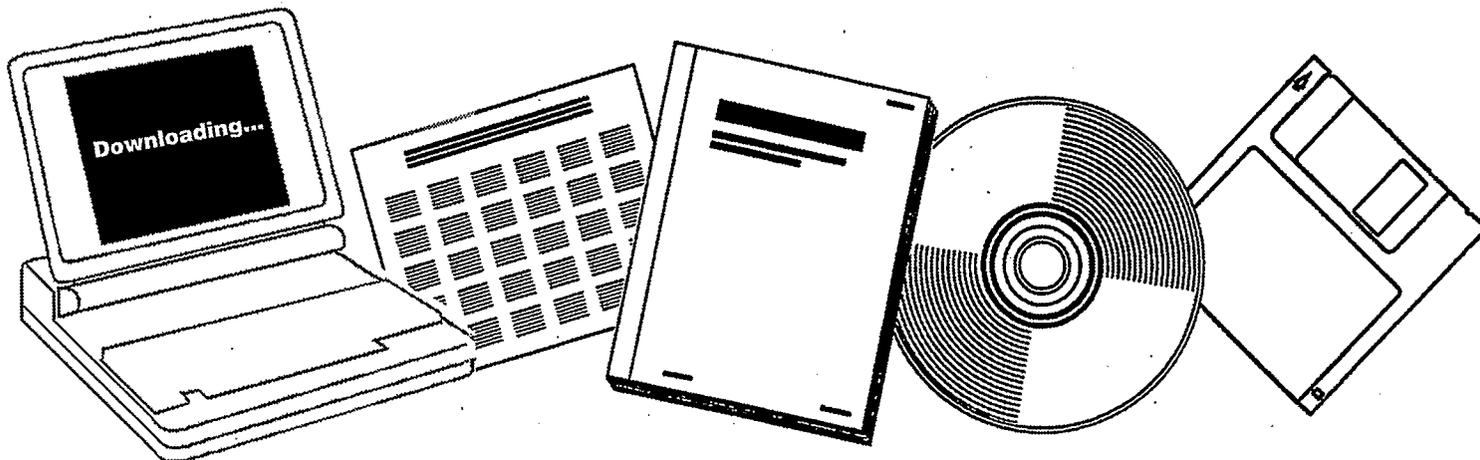
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**PROMOTION EFFECTS ON THE SYNTHESIS OF  
HIGHER ALCOHOLS. 11TH QUARTERLY REPORT,  
JANUARY-MARCH 1985**

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

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PROMOTION EFFECTS  
ON THE  
SYNTHESIS OF HIGHER ALCOHOLS

14th Quarterly Report

January 1984<sup>5</sup> - March 1984<sup>5</sup>

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April 1984<sup>5</sup>

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1984

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## 1. OBJECTIVE AND SCOPE OF WORK

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 shifts the products to higher alcohols. However, little is known about the effect of various alkali species on the catalysts components and the synthesis reaction. A series of research studies is planned which should greatly expand current knowledge in this area. In particular, the effect of various alkalis (Na, K, Rb, and Cs) on CO chemisorption, on the activity and selectivity for higher alcohol synthesis reaction, and on the deactivation characteristics of the catalyst will be determined for both supported metals (such as Pd and Pt) and mixed metal-metal oxide catalysts (such as Cu/ZnO and Cu/ZnO/Co). Direct measurement of electronic interactions between the alkali promoters and the other catalysts components will be attempted by ESCA.

This comprehensive research program involves members of the Departments of Chemical Engineering and of Chemistry. There is a great need for cooperation between researchers in the areas of catalysis and surface science. This research project seeks to accomplish this and utilize the resulting synergism in illuminating the precise function of alkali promotion in the higher alcohol synthesis.

## 2. SUMMARY OF PROGRESS

During the 11th quarter of the project, reaction pathways for the formation of oxygenated compounds and hydrocarbons from CO and  $H_2$  over group VIII metals has been studied. A better understanding of the reaction pathways for oxygenate formation would not only lead to a better way for the selective synthesis of higher alcohols but also provide an insight into the overall CO hydrogenation mechanism.

### 3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

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 oxygenate synthesis and hydrocarbon synthesis. The formation of these various products from CO and H<sub>2</sub> 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 (6,7). A number of reaction mechanisms consisting of various sequences of these elementary steps have been proposed to explain product formation during CO hydrogenation (1-9).

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 (5). 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 (10-15), (b) detecting the active sites for specific reactions (7,16,17), (c) determining secondary reactions of primary products (18,19,42), (d) elucidating reaction networks in an overall reaction (15,18,20-22), (e) determining the catalytic and chemical properties of the surface of a catalyst (23), and (f) determining the abundance of precursors to various products under synthesis conditions (24-29).

In order to gain a better understanding of the mechanism of CO hydrogenation, we have studied Ni/SiO<sub>2</sub> (a methanation catalyst), Ru/SiO<sub>2</sub> (a higher hydrocarbon synthesis catalyst), Rh/SiO<sub>2</sub> (a synthesis catalyst with a high selectivity for C<sub>2</sub> oxygenates), and Pd/SiO<sub>2</sub> (a methanol synthesis catalyst) by the addition of probe molecules to CO/H<sub>2</sub> 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 I-III. By determining the ability of a catalyst to catalyze these specific reaction steps, the reaction paths for the formation of hydrocarbons and oxygenates on these metal catalysts may be clarified.

## EXPERIMENTAL

### Catalyst Preparation and Characterization

Rh/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> were prepared via the incipient wetness method by impregnation of SiO<sub>2</sub> using aqueous solutions of the metal chloride. Ru/SiO<sub>2</sub> was prepared by ion exchange using Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>. Ni/SiO<sub>2</sub> was also prepared by the incipient wetness method using an aqueous solution of NiCO<sub>3</sub>. Following drying overnight in air at 40°C, the catalyst precursors were reduced in flowing H<sub>2</sub> on heating in 50°C steps (30 minutes) to 400°C and holding at that temperature for 16 hours. Prior to reaction, the catalysts were again reduced in flowing H<sub>2</sub> at 400°C for three hours. Average metal particle sizes for

these catalysts were determined by either x-ray diffraction line broadening using a MoK $\alpha$  radiation source or H<sub>2</sub> chemisorption. Metal loadings and average metal particle sizes for these catalysts are listed in Table IV.

#### Apparatus and Procedures

The apparatus used for this study is described elsewhere (19). The major parts of this apparatus consists of two saturators for feeding liquid vapor probe molecules (ethanol and acetaldehyde), gas flow controllers (H<sub>2</sub>, CO and He), a stainless steel microreactor containing 0.2-0.75 g of the catalyst in a furnace, an on-line GC using a 8 ft x 1/8" poropak Q column in series with a 6 ft x 1/8" 80/100 carbopak c/o.2% carbowax 1500 column, and an Apple II computer with an interface for automatic control. The CO hydrogenation and probe molecule studies were carried out at 300°C, 10 atm, CO/H<sub>2</sub> = 1, and space velocity of 700 to 1,100 hr<sup>-1</sup>. After more than 3 hours of just CO hydrogenation a small amount (1.1-3.3 mole %) of ethylene was added to the feed. It was continued for two hours then terminated. The reaction was carried out for another three hours to establish the reference data to estimate the rate of product formation that resulted from the ethylene addition. The increases in the rates of formation of certain products were assumed to be due to the reaction of ethylene with adsorbed CO, adsorbed H, and/or CO hydrogenation intermediates corresponding to reactions shown in Table I. By comparing the rates of product formation before, during, and after the addition of ethylene, the rates of hydrogenation, chain incorporation, and hydrocarbonylation of ethylene could be estimated. After the ethylene addition study, ethanol was added to CO/H<sub>2</sub> by passing CO/H<sub>2</sub> through a stainless steel saturator at room temperature. The composition of the mixture was determined by gas chromatography. The procedure and data treatment was similar to that of ethylene addition study. The addition of acetaldehyde was also studied in a similar manner except a slightly different

way of adding acetaldehyde to the CO/H<sub>2</sub> was used. Since acetaldehyde has a very high vapor pressure at room temperature, the acetaldehyde was added to CO/H<sub>2</sub> by using a He carrier flow of 2 cc/min to keep the concentration of added acetaldehyde under 2.5 mole % of the reactant mixture.

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.

## RESULTS

### CO Hydrogenation

The product distributions from CO hydrogenation over Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Pd/SiO<sub>2</sub> are listed in Table V. Ni/SiO<sub>2</sub> produced mainly methane with small amounts of C<sub>2+</sub> 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 (30). Ru/SiO<sub>2</sub> showed the highest selectivity to C<sub>2+</sub> hydrocarbons among these catalysts. Ruthenium is known to be one of the most active catalysts for the F-T synthesis (31,32). Numerous studies have reported that supported Ru catalysts, including Ru/SiO<sub>2</sub>, are able to produce significant amounts of higher hydrocarbons (31,31,32). Rh/SiO<sub>2</sub> exhibited a good selectivity to C<sub>2+</sub> oxygenated compounds with the production of only a small amount of methanol. Pd/SiO<sub>2</sub> showed a high selectivity for the formation of methanol. These results for Rh and Pd catalysts parallel those reported in the literature (18,33-35).

### Addition of Ethylene to CO/H<sub>2</sub>

The addition of ethylene to CO/H<sub>2</sub> 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 VI summarizes the increases in the rates of product formation as a result of ethylene addition.

Ni/SiO<sub>2</sub> appeared to demonstrate a moderate activity for the hydrogenolysis of ethylene to methane under synthesis conditions, while Ru/SiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Pd/SiO<sub>2</sub> 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 (16,18). CO on metals is known to affect both hydrogenolysis and hydrogenation (16), 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 (37), the selectivity for ethane was somewhat lower over Rh than over any of the other three catalysts. This can be readily understood by the fact that the CO insertion reaction to form C<sub>3</sub> oxygenated compounds (propionaldehyde and 1-propanol) competes with hydrogenation to form ethane over Rh/SiO<sub>2</sub> 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/H<sub>2</sub> over Pd/SiO<sub>2</sub> 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/SiO<sub>2</sub> and Ru/SiO<sub>2</sub>, and a noticeable increase in CO conversion was found for Rh/SiO<sub>2</sub> during the addition of ethylene to CO/H<sub>2</sub>.

#### Addition of Ethanol to CO/H<sub>2</sub>

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/SiO<sub>2</sub> was somewhat higher compared with the other cases (Table VII). The concentration of ethanol is known to affect its selectivity to diethyl ether, a compound, however, not stable at temperatures above 190°C (23). As shown in Table VII, Ru showed a strong activity and a high selectivity for the conversion of ethanol to C<sub>1</sub> and C<sub>2</sub> hydrocarbons as well as the apparent incorporation of ethanol into C<sub>3+</sub> hydrocarbons. Rh exhibited a moderate selectivity for the conversion of ethanol to C<sub>1</sub> and C<sub>2</sub> hydrocarbons but a relatively high selectivity for the incorporation of ethanol into C<sub>3</sub> 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.

#### Addition of Acetaldehyde to CO/H<sub>2</sub>

The product distributions and rates of acetaldehyde conversion during the addition of acetaldehyde to CO/H<sub>2</sub> are shown in Table VIII. In the case of Ni/SiO<sub>2</sub>, the selectivity for butyraldehyde was higher than that for C<sub>3</sub> oxygenated compounds indicating that the aldol condensation of acetaldehyde occurred on Ni/SiO<sub>2</sub> during the addition of acetaldehyde to CO/H<sub>2</sub>. In addition to the aldol condensation, Ni/SiO<sub>2</sub> also showed a fair selectivity for the decarbonylation of acetaldehyde to CH<sub>4</sub> and a high selectivity for the hydrogenation of acetaldehyde to ethanol. In contrast to Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub> and Rh/SiO<sub>2</sub> did not show aldol condensation activity. Rh/SiO<sub>2</sub> exhibited a strong

activity for the hydrogenation of acetaldehyde to ethanol. Ru/SiO<sub>2</sub> demonstrated a high activity in the decarbonylation of acetaldehyde to CH<sub>4</sub> and the conversion of acetaldehyde to C<sub>2</sub> hydrocarbons as well as the incorporation of acetaldehyde into C<sub>3+</sub> hydrocarbons.

## DISCUSSION

### Addition of Ethylene to CO/H<sub>2</sub>

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 I, 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<sub>x</sub> to form higher hydrocarbons, or may undergo hydrogenolysis to form methane. Among these three reactants (CO, H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>), adsorbed CO and adsorbed H are probably the most abundant species on the surface even in the presence of C<sub>2</sub>H<sub>4</sub>. 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 C<sub>3+</sub> hydrocarbons over Pd/SiO<sub>2</sub> is only slightly affected by the addition of ethylene to CO/H<sub>2</sub>, 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/SiO<sub>2</sub>, an increase in CO conversion during the addition of ethylene to CO/H<sub>2</sub> was observed for Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub> and Rh/SiO<sub>2</sub>. This appears to be due to the reaction of ethylene with adsorbed CO (36).

All group VIII metals are known to be active in catalyzing both CO hydrogenation and ethylene hydrogenation (3,37), both involving C-H bond formation. They also involve different reaction steps and active site requirements (3,37), so that the activity for ethylene hydrogenation does not parallel that of CO hydrogenation over these metals.

As shown in Table VI, hydrogenolysis of ethylene only occurred on the Ni/SiO<sub>2</sub> catalyst. A similar observation has been reported by van Barneveld (7).

The capability of group VIII metals to dissociate CO has been well established in the literature (38,39). CO dissociation activity decreases in the order: Ni/SiO<sub>2</sub> > Ru/SiO<sub>2</sub> > Rh/SiO<sub>2</sub> > Pd/SiO<sub>2</sub>. 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 C<sub>3</sub> oxygenates (propionaldehyde and propanol) (19,40), the low selectivity of ethylene toward C<sub>3</sub> oxygenates over Pd/SiO<sub>2</sub> 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 C<sub>3</sub> oxygenates from ethylene. It is likely that the selectivity for the conversion of ethylene to C<sub>3</sub> 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 VI). A similar

observation has also been reported by van Barneveld (7). 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 (10,42).

#### Addition of Ethanol to CO/H<sub>2</sub>

Adsorbed ethanol has been identified in the form of an ethoxy group on Fe (43) and Pt (44), and it can react to produce CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. In the presence of CO/H<sub>2</sub>, the adsorbed ethanol and its decomposition products may react with CO hydrogenation intermediates resulting in a variety of products (Table II). As shown in Table VII, both Ni/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> 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 (3), 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 (23).

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 C<sub>1</sub> and C<sub>2</sub> hydrocarbons were observed. As with Fe (20,21), 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 (20,21) 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  $C_{3+}$  hydrocarbons has been observed to be very low for both of these metal catalysts. The formation of a significant amount of  $C_3$  oxygenated compounds (propanol and propionaldehyde) during the addition of ethanol to  $CO/H_2$  over  $Rh/SiO_2$  may be also explained by dehydration of ethanol followed by CO insertion. Reactions 7 and 8 of Table II are also possible on these metal catalysts, but there is no definite evidence for these reactions.

#### Addition of MeCHO to $CO/H_2$

Adsorbed acetaldehyde has been found to readily form ethoxy intermediates on Fe (45). 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  $CO/H_2$  as happened over  $Ni/SiO_2$  and  $Ru/SiO_2$ . In contrast, the addition of ethanol to  $CO/H_2$  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  $Ni/SiO_2$ . Aldehydes have a great tendency to undergo the aldol condensation but it is not clear why this occurs mostly on the  $Ni/SiO_2$  catalysts.

A small amount of acetone was observed during the addition of acetaldehyde to  $CO/H_2$  over  $Ni/SiO_2$ ,  $Ru/SiO_2$ , and  $Rh/SiO_2$ . This could proceed

through dehydrogenation of the acetaldehyde to acyl intermediates followed by their association with  $\text{CH}_3$  species to produce acetone (41,48). In fact, by isotopic tracing experiments, this latter step has already been shown, to occur (41).

### Reaction Mechanisms

The selectivities for the various probe molecule reactions are summarized in Table IX. Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, Rh/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> 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 (1-49) are summarized in Figure 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/SiO<sub>2</sub> appear to be unfavorable for the formation of higher hydrocarbons and oxygenated compounds. Ru/SiO<sub>2</sub>, a good higher hydrocarbon synthesis catalyst, demonstrated a strong catalytic activity for ethylene hydrogenation, conversion of ethanol to C<sub>1</sub> and C<sub>2</sub> 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 C<sub>2+</sub> oxygenated compounds, and they exclude oxygenated intermediates as major intermediates for hydrocarbon chain growth over Ru/SiO<sub>2</sub>. Rh/SiO<sub>2</sub>, a good C<sub>2</sub> oxygenate synthesis

catalyst, exhibited strong catalytic activity for the incorporation of ethylene and ethanol to  $C_3$  oxygenated compounds, but poor catalytic activity for decarbonylation 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/SiO<sub>2</sub>, 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/SiO<sub>2</sub> is somewhat similar to those displayed by Ni/SiO<sub>2</sub>. They do not favor the formation of  $C_{2+}$  species.

#### CONCLUSIONS

The synthesis of oxygenated compounds and hydrocarbons over Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Pd/SiO<sub>2</sub> would appear to follow different reaction paths resulting in different product distributions at 10 atm. The formation of  $C_{2+}$  oxygenated compounds over Rh/SiO<sub>2</sub> 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<sub>x</sub> into C<sub>y</sub>H<sub>x</sub> appears to be a major route for the formation of higher hydrocarbons over Ru/SiO<sub>2</sub>. The inability of Ni/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> 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 1) should provide a deeper insight into the mechanism of product formation over the Group VIII metals.

4. FORECAST OF WORK

During the 12th quarter, a final report of this project will be prepared.

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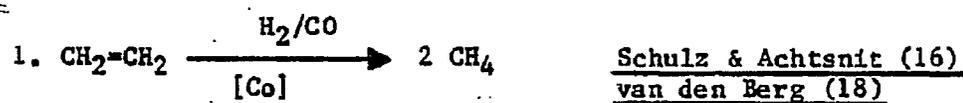
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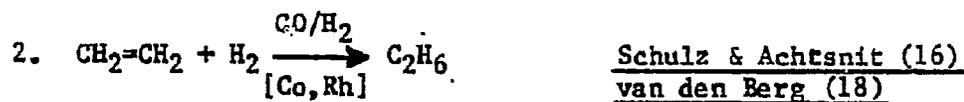
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**Table I: Possible Reactions due to Ethylene Addition during CO Hydrogenation**

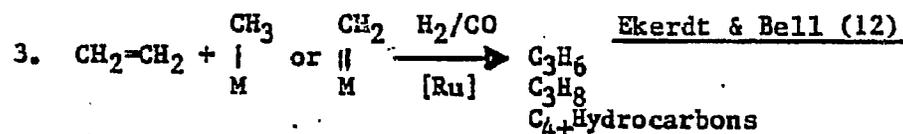
Formation of CH<sub>4</sub>



Hydrogenation



Chain Growth



CO Insertion

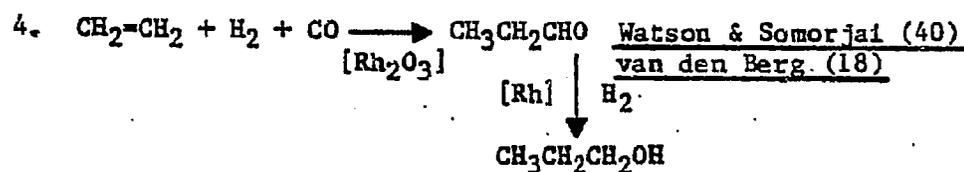


Table II: Possible Reactions due to Ethanol Addition During CO Hydrogenation

Formation of CH<sub>4</sub> or C<sub>2</sub> Hydrocarbons

1.  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[\text{Fe}(100)]} \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6$  Benziger & Madix (43)
2.  $\text{C}_n\text{H}_{2n+1}\text{OH}(\text{ad}) \xrightarrow{[\text{Pt}]} \text{C}_n\text{H}_{2n+1}\text{OH}(\text{g})$   
 $\text{CO}(\text{ad}) + 2(n+1)\text{H}(\text{ad}) + n\text{C}(\text{ad})$   
 $\text{CO}(\text{ad}) + \text{C}_{n-1}\text{H}_{2n-3}(\text{ad}) + 5\text{H}(\text{ad})$   
Redulic & Sexton (44)
3.  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[\text{oxide cat.}]} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$  Krylov (46)
4.  $\text{RCH}_2\text{OH} \xrightarrow{[\text{Ni}]} \text{RCH}_2\text{CHO} + \text{H}_2$  Pines (23)  
 $\text{RCH}_2\text{CHO} \xrightarrow{[\text{Ni}]} \text{RCH}_3 + \text{CO}$   
 $\text{CO} + 3\text{H}_2 \xrightarrow{[\text{Ni}]} \text{CH}_4 + \text{H}_2\text{O}$

Chain Growth

5.  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[\text{Fe}], \text{CO}/\text{H}_2} \text{C}_3+\text{ Hydrocarbons}$  Kummer & Emmett (21)

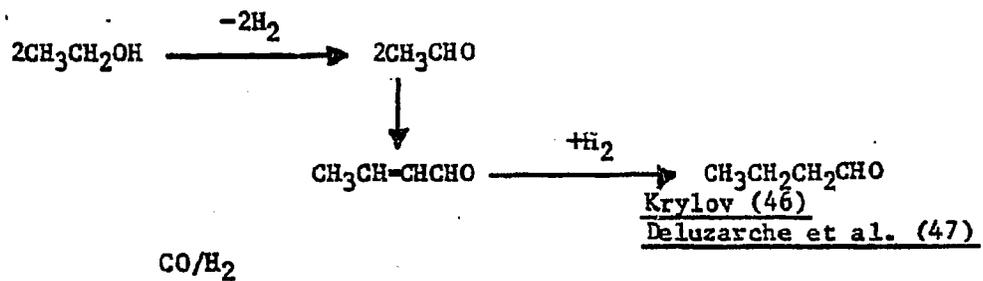
Dehydrogenation

6.  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[\text{oxide cat.}]} \text{CH}_3\text{CHO} + \text{H}_2$  Krylov (46)

Formation of C<sub>3</sub> Oxygenates

7.  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{M} \end{array} + (\text{CH}_3\text{CH}_2\text{OH})_{\text{ad}} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  Rofer-DePoorter (5)
8.  $\begin{array}{c} \text{nCH}_2 \\ | \\ \text{M} \end{array} + \begin{array}{c} \text{CH}_2\text{CHO} \\ || \\ \text{M} \end{array} \xrightarrow{\text{H}} \text{CH}_3(\text{CH}_2)_n\text{CHO}_{\text{ads}}$  Hackenbruch et al. (49)

9. Formation of C<sub>4</sub> Oxygenates





**Table IV: Metal Particle Size of Ni/SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, Rh/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>**

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

<sup>a</sup>measured by hydrogen flow chemisorption at 25°C.

<sup>b</sup>determined by x-ray diffraction.

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

**Table V: Activity and Product Selectivity (mol. %)**  
during CO Hydrogenation

	20 wt% Ni/SiO <sub>2</sub>	1.8 wt% Ru/SiO <sub>2</sub>	3 wt% Rh/SiO <sub>2</sub>	2.3 wt% Pd/SiO <sub>2</sub>
r <sub>CO</sub> (moles/kg/hr)	0.91	5.06	1.3	2.7
% CO Conv.	0.16	3.4	0.88	0.5
CH <sub>4</sub>	82.8	76.5	41.2	0.9
C <sub>2</sub>	12.8	8.5	6.8	1.4
C <sub>3</sub> +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 <sub>3</sub> OX	0.14	0.3	16.6	0.14
Acetone				
Butyraldehyde	0.03	0	0.6	0
EtOAc				

(300°C, 10 atm, CO/H<sub>2</sub> = 1)

OX: Oxygenated Compounds

HC: Hydrocarbons

**Table VI: Product Selectivity (mol. %) from Ethylene Reaction During CO Hydrogenation**

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

(300°C, 10 atm, CO/H<sub>2</sub> = 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

**Table VII: Product Selectivity (mol. %) from Ethanol Reaction during CO Hydrogenation**

	20 wt% Ni/SiO <sub>2</sub>	1.8 wt% Ru/SiO <sub>2</sub>	3 wt% Rh/SiO <sub>2</sub>	2.3 wt% Pd/SiO <sub>2</sub>
Selectivity (mol%)				
CH <sub>4</sub>	0	74.6	15.1	0.7
C <sub>2</sub>	0	10	2.1	4.2
C <sub>3+HC</sub>	1.8	13.2	3.0	3.3
MeOH	0	0.5	6	0(b)
MeCHO	91	1.4	20.8	87.6
C <sub>3</sub> 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) w	(0.99) 0.81	(4.9) 4.6	(1.10) 1.24	(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/H<sub>2</sub> = 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

**Table VIII: Product Selectivity (mol. %) from Acetaldehyde Reaction During CO Hydrogenation**

	20 wt% Ni/SiO <sub>2</sub>	1.8 wt% Ru/SiO <sub>2</sub>	3 wt% Rh/SiO <sub>2</sub>
Selectivity (mol%)			
CH <sub>4</sub>	13	60.7	4.8
C <sub>2</sub>	1.1	10.0	0.3
C <sub>3</sub> +HC	4.3	9.6	3.2
MeOH	0	0	0
EtOH	68	19.1	86
C <sub>3</sub> 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 <sub>CO</sub> <sup>(a)</sup> (w/o)	(0.68)	(4.9)	(1.32)
w	1.39	3.0	1.32
% HAc added	0.87	2.4	0.73
r <sub>A</sub> <sup>(a)</sup>	4.4	6.7	1.56
% HAc conv.	46	95.3	73

300°C, 10 atm, CO/H<sub>2</sub> = 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

**Table IX: Selectivities of the Probe Molecule Reactions**

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

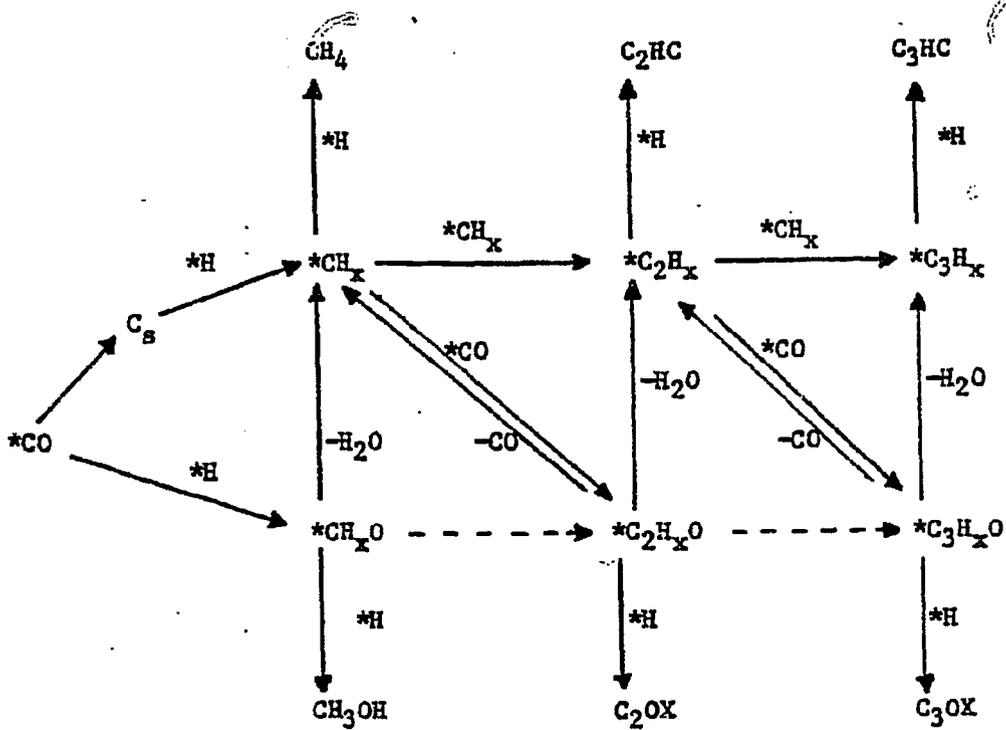
(300°C, 10 atm, CO/H<sub>2</sub> = 1)

+++ : strong (&gt; 10% of probe reactant incorporated)

++ : moderate (&gt; 5%)

+ : weak (&gt; 1%)

0 : inactive (&lt; 1%)



**Figure 1:** Possible Reaction Network for CO Hydrogenation

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