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The Investigation of Methanation Kinetics Over Ruthenium and Iron-Ruthenium Bimetallic Catalysts.

Krisda Chirapongse
Louisiana State University and Agricultural & Mechanical College

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THE INVESTIGATION OF METHANATION KINETICS OVER RUTHENIUM AND IRON-RUTHENIUM BIMETALLIC CATALYSTS

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The Investigation of Methanation Kinetics over
Ru and Fe-Ru Bimetallic Catalysts

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by

Krisda Chirapongse
B.S. Ch.E., The University of Missouri, 1979
M.S. Ch.E., Louisiana State University, 1981
August 1984
This dissertation is dedicated to

The Honorable Max Schwabe,
whose devotion to his family and to his country
inspired those around him.

Without his love and understanding,
this work would not have been possible.
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ABSTRACT

The catalytic properties of Ru and Fe-Ru bimetallics supported on Y-Zeolite were determined for the CO hydrogenation reaction. The results, based on the reaction at 523 K and an H₂:CO ratio of 3:1, revealed that the addition of Fe to Ru effectively reduces the number of both H₂ and CO active sites as determined by chemisorption experiments. Based on H₂ chemisorption, the dispersion (number of active sites per total number of metal atoms) decreased from 0.59 with no Fe present to 0.02 with 5.9% Fe. This phenomenon was substantiated by the ESCA analysis which indicated totally reduced Ru metal particles in both Ru and Fe-Ru bimetals, however iron oxides could not be reduced to their metallic state.

The addition of Fe also influences the product distribution. An increase in Fe content reduces the amount of methane while increasing the amount of long chain hydrocarbons. Furthermore the product distribution follows the Schultz-Flory distribution. This observation is probably due to surface H₂ deficiency encouraging chain propagation instead of chain termination. The rate determining step is the hydrogenation of surface methylene species.

The infrared analysis of CO adsorption on Ru catalyst at 373 K indicates 3 types of adsorption: bridge adsorption at 1950 cm⁻¹, linear adsorption at 2046 cm⁻¹, and
multiple adsorption at 2089, 2102, 2137, and 2157 cm\(^{-1}\). However under methanation reaction conditions at 523 K, it was found that the surface of the catalyst was saturated by linearly adsorbed CO around 2000 cm\(^{-1}\). The infrared experiments as well as the isotopic dilution experiment point to surface segregation where Ru and Fe do not enter into a solid solution. Finally, the addition of Fe to Ru catalysts produces neither a geometrical nor an electrical effect on Ru atoms.
I - INTRODUCTION

The successful production of gaseous and liquid hydrocarbons from coal requires an efficient and selective hydrogenation of carbon to the desired hydrocarbons. The usual and most promising method is the production of synthesis gas (H$_2$/CO mixture) via the steam reforming of coal followed by the catalytic reaction of this mixture to give the desired products. This last step requires a catalyst which is effective, selective, and resistant to sulfur poisoning. Several basic studies [11,12,17,22] have indicated that the Group VIII metals all act as synthesis gas hydrogenation catalysts with Ru and Fe exhibiting the highest activity. At a moderate pressure, Ru and Fe catalysts convert synthesis gas to mostly methane, but significant quantities of C$_2$ to C$_5$ hydrocarbons are also observed.

In the manufacture of methane, a synthesis gas mixture containing H$_2$ and CO with H$_2$/CO ratio in the vicinity of 3/1 is passed over a series of reactors maintained at moderate pressure and temperature to provide a product which is essentially methane and a small amount of other hydrocarbons. It is well known that the homogeneous reaction of CO and H$_2$ is feasible at high temperature, however the reaction is slow, therefore a catalyst is needed to increase the rate. At the present time, the focus of this process has been concentrated on the improvement of
the catalysts (both in selectivity and activity) and the process. A good catalyst is one which can maintain high activity over long periods of operation, can resist poisoning, and has high selectivity toward long chain hydrocarbons.

A. PREVIOUS WORK ON CATALYTIC METHANATION

A great deal of research has been conducted on the catalytic synthesis of organic materials from CO and $\text{H}_2$ since it was first reported by Sabatier [1]. At the turn of the century, Sabatier produced methane from synthesis gas using a nickel catalyst. The mechanism of hydrogenation of carbon monoxide to higher hydrocarbons has been the subject of an extensive study for many years, led by the early studies of Fischer and Tropsch [2]. The subsequent studies have identified active catalysts as the transition elements with unfilled 3d, 4d and 5d orbitals: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt, as well as some elements that can assume these configurations (e.g., Ag).

Even though there have been numerous works done on this synthesis, results have not successfully described all of the mechanisms of the hydrogenation of carbon monoxide. This is also true for the simplest hydrocarbon synthesis reaction—methanation—which is not completely understood. There have been various kinetic models proposed to describe the methanation reaction [3-8], but none have been widely accepted by the scientific community. Therefore, a fundamental understanding of the simplest reaction should
help us to learn more about the more complex hydrocarbon synthesis.

1. Chemistry and Thermodynamics

When the hydrogen to carbon monoxide ratio in synthesis gas is equal to or greater than 3, the conversion of CO and H\textsubscript{2} to methane and higher molecular weight hydrocarbons is likely to occur. The methanation reaction can be described as:

\[ 3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O} \] (1).

Methane is also formed by hydrogenation of carbon oxides in two other reactions:

\[ 2\text{H}_2 + 2\text{CO} \rightarrow \text{CH}_4 + \text{CO}_2 \] (2)
\[ 4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \] (3).

Also, reaction 2 can be considered to be the combination of reaction 1 and the water-gas shift reaction 4. There is also another reaction, reaction 5, which is the dissociation of CO into carbide, which can significantly alter the nature of catalysts.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \] (4).
\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \] (5).

Although the water-gas shift reaction does not produce methane, it is an important reaction in methanation chemistry, altering the H\textsubscript{2}/CO ratio with far reaching effects on reaction products.

The free energies of all the above reactions have a large negative values for a wide range of temperatures.
However, the reactions are relatively slow and hence, catalysts are needed to alter the rate of the reactions. It is observed that all the reactions are exothermic and, indeed, all except reaction 4, are highly exothermic. It should be noted that heats of reaction are not strongly influenced by temperature. In contrast, changes in free energy and equilibrium constants for methanation reactions are quite dependent on temperature.

The thermodynamics of hydrogenation of CO have been extensively described in numbers of publications [9,10]. Briefly, the properties of these reactions can be summed up as follows:

1. All the reactions forming hydrocarbons from H\(_2\) and CO are exothermic; the free energy changes of the reactions increase and the equilibrium constants decrease with temperature;

2. The formation of methane has the most negative free energy change per carbon atom;

3. Below 623 K most of the reactions have equilibrium constants above unity, while above 673 K, nearly all of the synthesis reactions become thermodynamically unfavorable, with the exception of methanation, for which the equilibrium constant exceeds one up to 923 K;

4. Equilibrium methane yields are affected critically by temperature and by H\(_2\)/CO ratios. Methane production is highest at lower
temperatures and higher ratios;

5. The hydrogenation of CO$_2$ to hydrocarbons is thermodynamically more favorable than the hydrogenation of CO;

6. Reactions of CO and H$_2$ with methane to form higher hydrocarbons are thermodynamically feasible; and,

7. The formation of olefins is slightly less favored than that of paraffins. Reactions to cyclohexane and methylcyclohexane have equilibrium constants very near those for n-hexane and n-heptane respectively.

2. Kinetics

Even though there has been a tremendous amount of research done on the kinetics of the hydrogenation of CO since the time of its first observation, most of the works [6,11-14] were performed prior to the advent of spectroscopic equipment and particularly, the methods of determining the characteristics of the catalysts such as metal dispersion and crystallite size. Most of the works were performed with a high conversion (using integral methods) which revealed insignificant kinetic information, because at high conversion there are number of competing secondary reactions which affect the main reaction. Finally, without the catalytic properties presented, these works have no basis for comparison. Some of the results of these experiments are summarized in Table I-1.
Recent investigations [15-19] on the hydrogenation of CO have included chemisorption measurements which provide a measure of the reduced metal surface area. This technique provides an insight into the characteristics of the metal particle on the support such as the crystallite size and the dispersion of metal on the surface of the support. Thus for the first time "specific activities", rate per unit metal surface area which is typically determined by hydrogen chemisorption, have been calculated for these synthesis reactions. The results of selected works are presented in Table 1-2. All kinetic data were obtained from differential reactors which reveal promising kinetic information. The result from differential reactors represented the rate of reaction defined at very low conversion, therefore the turnover number for methane formation (molecules of CH₄ formed per surface metal site per second) was independent of space velocity. The other benefits of a differential reactors include the minimization of heat and mass transfer effects, the elimination of any significant effects due to product inhibition, and determination of the initial rate without the complication of secondary effects [17,20]. Perhaps the most noticeable result is the consistency of the specific activity in the methanation reaction, expressed here as a turnover number. The data from various laboratories agree within a factor of approximately two when identical pressures and temperatures are compared.
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<td>156</td>
<td>13</td>
</tr>
<tr>
<td>Fe-metal</td>
<td>498-538</td>
<td>6-12</td>
<td>1-8</td>
<td>r=kH₂P₂</td>
<td>70</td>
<td>14</td>
</tr>
</tbody>
</table>
TABLE II-2
Specific Activities and Kinetic Behavior of Various Metals in the Methanation Reaction

\[ r = A \exp \left( -\frac{E_{CH_4}}{RT} \right) P_{H_2}^{\alpha} P_{CO}^{\beta} \]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. K</th>
<th>Pressure of H₂+CO, kPa</th>
<th>( \frac{H_2}{CO} )</th>
<th>( E_{CH_4} ) kJ/mole</th>
<th>( x )</th>
<th>( y )</th>
<th>( N_{CH_4} ) at 548K ( \quad \text{Sec}^{-1} \times 10^3 )</th>
<th>( N_{CO} ) at 548K ( \quad \text{Sec}^{-1} \times 10^3 )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0% Ni/Al₂O₃</td>
<td>473-508</td>
<td>103</td>
<td>3</td>
<td>109</td>
<td>0.8</td>
<td>-0.2</td>
<td>85</td>
<td>128</td>
<td>15</td>
</tr>
<tr>
<td>2% Ni/Al₂O₃</td>
<td>523</td>
<td>77</td>
<td>3</td>
<td>130</td>
<td>-</td>
<td>-</td>
<td>90</td>
<td>220</td>
<td>16</td>
</tr>
<tr>
<td>5% Ni/Al₂O₃</td>
<td>503-528</td>
<td>103</td>
<td>3</td>
<td>105</td>
<td>0.8</td>
<td>-0.3</td>
<td>37</td>
<td>44</td>
<td>17</td>
</tr>
<tr>
<td>1.5% Ru/Al₂O₃</td>
<td>473-613</td>
<td>77</td>
<td>3</td>
<td>100</td>
<td>1.8</td>
<td>-1.1</td>
<td>20</td>
<td>59</td>
<td>18</td>
</tr>
<tr>
<td>5% Ru/Al₂O₃</td>
<td>478-503</td>
<td>103</td>
<td>3</td>
<td>101</td>
<td>1.6</td>
<td>-0.6</td>
<td>181</td>
<td>325</td>
<td>17</td>
</tr>
<tr>
<td>15% Fe/Al₂O₃</td>
<td>498-528</td>
<td>103</td>
<td>3</td>
<td>90</td>
<td>1.1</td>
<td>-0.1</td>
<td>57</td>
<td>160</td>
<td>17</td>
</tr>
<tr>
<td>10% Ru/SiO₂</td>
<td>473-573</td>
<td>103</td>
<td>3</td>
<td>101.2</td>
<td>1.5</td>
<td>-0.6</td>
<td>893</td>
<td>---</td>
<td>19</td>
</tr>
</tbody>
</table>
Dalla Betta et al. [18] utilized a differential batch reactor to study the initial rate of CO hydrogenation at 0.75 atm. It was assumed that there was no loss of metal sites under the conditions of the reaction, hence the hydrogen adsorption technique was used in determining the dispersion and the particle size. They found that the initial reaction rate on an Ru/Al$_2$O$_3$ catalyst was independent of the Ru particle size from less than 10 to 90 Å. In a subsequent study, Dalla Betta et al. [16] employed a single pass flow reactor in addition to a differential reactor. Both initial and steady-state reaction rates of CO hydrogenation were obtained for 2% Ni/Al$_2$O$_3$, 5% Ni/ZnO$_2$, Raney Ni, and 1.5% Ru/Al$_2$O$_3$ catalysts. The initial rates at 548 K are listed in Table I-2. Steady-state reaction rates were also measured at 673 K, and the Ru/Al$_2$O$_3$ catalysts were found to be an order of magnitude less active than predicted by extrapolation of the initial rate data. The lower activities were attributed to carbon deposits on the surface of the catalyst.

Vannice [15,17,8,20,21] has studied various Group VIII metal supported catalysts by using a differential reactor. In his first study [17], he found that the turnover number of the most active metal (Ru), is only 2 orders of magnitude larger than the least active metal (Ir). Later on [22], with chemisorption information, he determined that the ordering of these metals according to the average molecular weight of their hydrocarbon products gives the
following sequence: Ru>Fe>Co>Rh>Ni>Ir>Pt>Pd. The sequence is different when the metals are ranked according to their specific activities. The only other comparison of the catalytic behavior of the Group VIII metals in a single study is that conducted by Fischer and co-workers in 1925 [22]. Expressing activity as the rate of methane production per gram of metal, they ranked these unsupported metal catalysts in order of decreasing activity as follows: Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Pd. These two rankings are compared in Table 1-3.

The differences in relative activity between Vannice [17] and Fischer, et al. [22], are most likely due to the rate normalization of the number of active sites on the surface. However, with supported metals, one must be aware of metal particle size effects and metal support interactions that may alter the catalytic behavior. Some of these supported metals (Ru, Fe, Co, Ni) had average crystallite sizes that were quite large (>100 A) and their catalytic behavior might be parallel to the unsupported metal. In contrast, some of the metals (Rh, Pt, Ir, Pd) have high dispersion with very small size (<100 A). In these cases, the two possible support interactions mentioned above might cause the metals to behave quite differently from their corresponding metals.

These results are generally in good agreement with the recent works by Karn, et al. [23], Randhava and co-workers [13], McKee [11] and Shultz, et al. [25]. Karn, et
Fischer, et al. [22]
(Ranked as rate/gm of metal)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fischer</th>
<th>Vannnice Study [17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>Highest</td>
<td>Ru</td>
</tr>
<tr>
<td>Ir</td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Rh</td>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>Rh</td>
</tr>
<tr>
<td>Os</td>
<td></td>
<td>Pd</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Fe</td>
<td>Lowest</td>
<td>Ir</td>
</tr>
</tbody>
</table>

Turnover Number $\times 10^3$

- Ru: 181
- Fe: 57
- Ni: 32
- Co: 20
- Rh: 13
- Pd: 12
- Pt: 2.7
- Ir: 1.8

Table I-3. Group VIII Metal Activity at 543 K for the Methanation Reaction
al. [23] found that 0.5% Ru/Al$_2$O$_3$, yielded an apparent activation energy of 152.2 kJ/mole for the methanation reaction. They also reported diffusion control at high conversions. McKee [11] examined the behavior of unsupported Ru in the CO-H$_2$ reaction and found it to be more active than Rh, Ir, Pt or Pd. Similarly, Shultz, et al. [12], found the relative activities of Group VIII metals, based on conversion, to decrease in the following order: Ru, Rh, Os, Pt, Pd.

In another study by Vannice [15], the behavior of Ni on a variety of supports was examined. A factor of 5 existed between turnover numbers measured on different catalysts at 548 K, but no trend associated directly with support properties was apparent. Compared to Pt or Pd, Ni appears to be less sensitive to the support properties or to differences in metal particle size [15]. Vannice [20] found that a reduction in particle size enhanced the specific activity of Pt in the methanation reaction by two orders of magnitude. Pd particles showed an improvement in the rate when the dispersion was high. However, King [26], found that the specific activity for both CO conversion and CH$_4$ production with a supported Ru catalyst increases with increasing metal particle size. The same results may be obtained by either increasing the metal loading on a given support or by choosing a support which poorly disperses the metal. Furthermore, the supported catalysts with large particles are similar to unsupported Ru in activity, but not
in selectivity. Product selectivity is characterized by olefin/paraffin ratio, length of the hydrocarbon chain, and tendency to produce branched-chain hydrocarbons. This conclusion is in good agreement with the previous work of Dalla Betta, et al. [16] who found an increase in steady-state activity with increasing particle size for Ru/Al₂O₃ catalysts. Finally, Bell concluded that the degree of saturation of the products increases with increasing CO conversion. The length of the hydrocarbon chain is dependent upon temperature, pressure, and nature of the support, but not on the degree of CO conversion. Branch-chain hydrocarbons are produced utilizing acidic supports such as silica-alumina or zeolites, by subsequent isomerization of the initially formed straight-chain products. Bell also suggested that the support may alter the catalytic behavior of Ru through both electric and dispersion effects.

Vannice [17] also points out a correlation between the CO heat of adsorption and the activity of the catalysts. He concluded that the most active metals are those with the weakest CO-metal adsorption bond (linear form) as opposed to the more strongly adsorbed CO (bridge form).

These recent studies provide for the first time the turnover number which allows various laboratories to compare their results with a common basis. These results also give the specific activity data, as well as the measurement of the dispersion of metal on the catalyst. The latter value yields the basis for comparison of various catalyst
supports. The information on the states and characteristic properties of metal-loaded catalysts have greatly enhanced the understanding of the kinetics.

3. Mechanism

The mechanism of the hydrogenation of carbon monoxide to higher hydrocarbons has been the subject of intensive study for many years. Unfortunately, there are very few works on the most simple reaction—methanation. Most of the research has been concentrated on the production of long-chain hydrocarbons under the conditions of the Fischer-Tropsch reaction. Here, in contrast to methane synthesis, the mechanism of chain growth is of importance. Despite these considerations, the fact that somewhat different catalysts and different reactions and conditions are used to optimize higher hydrocarbon formation, many considerations in Fischer-Tropsch synthesis are believed applicable to the methanation synthesis.

At this time, there are basically two schools of thought about the possible mechanism of the hydrogenation of CO. One of the earliest proposals for the hydrocarbon synthesis was the carbide theory proposed by Fischer and Tropsch [2]. The carbide theory in its simplest form postulates that adsorbed carbon monoxide is reduced to surface metal carbide. The surface carbide was believed to be hydrogenated and the adsorbed methylene radicals polymerize into adsorbed olefinic and paraffinic hydrocarbons. The other school of thought is led by Vannice
who postulates that the methanation reaction is a function of the concentration of weakly bound CO on the surface. The postulated reaction mechanism involves the formation of partially hydrogenated CO molecules. This oxygenated intermediate could yield methane via complete hydrogenation or higher molecular weight species could be produced via successive CO insertion followed by hydrogenation.

The oxygenated postulate has been widely studied in the past two decades in an attempt to explain the formation of methanol or formaldehyde from the same catalysts used for methanation, but with different operating conditions. However, attempts to detect formaldehyde or methanol during the synthesis of methane on Ni catalysts were unsuccessful [16]. Moreover, when methanol was used as a starting material over a cobalt catalyst, it was shown that the yield of hydrocarbons was much less than if the reaction was started with CO and H\textsubscript{2}. There are a number of proposed mechanisms at the present time and a few selected mechanisms are presented in Figures I-1 thru I-7. Several workers have concluded that the synthesis based on CO and H\textsubscript{2} involves the production of an unstable intermediate complex containing C, H, and O atoms, which is the precursor to both hydrocarbons and alcohols.

At present, two related mechanisms deserve special consideration. Both involve the initial formation of a HCOH surface complex, but they are different in sequential steps. One mechanism involves methylene radical intermediates and
Figure I-1. Mechanism Proposed by Vlasenko and Yuzefovich [28].
Initiation of Chain
\[ \text{O} + 2\text{H} \rightarrow \text{C} - \text{OH} \] (1)

Propagation
\[ \text{C} - \text{OH} + \text{C} - \text{OH} \rightarrow \text{C} - \text{C} - \text{OH} + 2\text{H} \rightarrow \text{C} - \text{OH} \] (2)

Growth of Chains
a) at end carbon
\[ \text{R} - \text{OH} + 2\text{H} \rightarrow \text{R} - \text{CH} = \text{C} - \text{OH} \] (3)

b) at penultimate carbon
\[ \text{CH} = \text{C} - \text{OH} \rightarrow \text{CH} - \text{C} - \text{OH} \rightarrow \text{CH} - \text{C} - \text{OH} \rightarrow \text{CH} - \text{C} - \text{OH} \] (4)

Termination of Chain
\[ \text{R} - \text{CH} = \text{C} - \text{OH} \rightarrow \text{RCH}_2\text{CHO} \text{ Acids, esters, and alcohols} \] (5)
\[ \text{RCH}_2\text{OH} \rightarrow \text{RCH} = \text{C} - \text{OH} \text{ Hydrocarbons} \] (6)

Methane Synthesis
\[ \text{C} + 2\text{H}_2 \rightarrow \text{C} = \text{C} \rightarrow \text{C} = \text{C} \rightarrow \text{CH}_4 \] (7)

Figure 1-2. Mechanism Proposed by Storch, Golumbic, and Anderson [10,29].
Figure I-3. Mechanism Proposed by Bousquet et al. [4].

\[
\begin{align*}
CO + H_2 + 2S &\rightarrow H_OH \\
C &\rightarrow CH_4 + 2S
\end{align*}
\]  (1)

Figure I-4. Mechanism Proposed by Van Herwijnen et al. [5].

\[
[H_2CO]_{ADS} + H_2_{ADS} \rightarrow CH_2_{ADS} + H_2O_{ADS} \text{ (RDS)}
\]  (1)

Figure I-5. Mechanism Proposed by Schoubye [6].

\[
\begin{align*}
H_2S &\rightarrow 2H'_{ADS} \\
H_2 + 2S &\rightarrow 2H''_{ADS}
\end{align*}
\]  (1)
\[ \text{CO} + \text{S} \rightleftharpoons \text{S-CO} \]  
(1)

\[ \text{H}_2 + 2\text{S} \rightleftharpoons 2\text{S-H} \]  
(2)

\[ \text{S-H} + \text{S-CO} \rightleftharpoons \text{S-HCO} + \text{S} \]  
(3)

\[ \text{S-H} + \text{S-HCO} \rightarrow \text{S-H}_2\text{CO} + \text{S} \]  
(4)

\[ \text{S-H} + \text{S-H}_2\text{CO} \rightleftharpoons \text{S-H}_3\text{CO} + \text{S} \]  
(5)

\[ \text{S-H}_3\text{CO} \rightarrow \text{products} \]  
(6)

Figure I-6. Mechanism Proposed by Fontaine [7].

\[ \text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{CO}_{\text{ADS}} \]  
(1)

\[ \text{H}_2\text{CO}_{\text{ADS}} + \frac{y}{2}\text{H}_2\text{ADS} \rightarrow \text{CH}_y\text{ADS} + \text{H}_2\text{O} \text{ (RDS)} \]  
(2)

\[ \text{CH}_y\text{ADS} + \text{H}_2\text{ADS} \rightarrow \text{CH}_4\text{ADS} \]  
(3)

Figure I-7. Mechanism Proposed by Vannice [8]
emphasizes electronic charge or polarization factors.

Vlasenko [28] concluded that the most probable process for the methanation reaction on Ni, Co, and possibly Fe catalysts are steps 1 thru 5 in Figure I-1, with the third step being the rate determining step (RDS). He assumed that highly charged surface species are formed during adsorption. For the synthesis of higher hydrocarbons, the fifth stage of the scheme is not the reaction of methylene radicals with hydrogen, but their polymerization. This result is further supported by Eidus [34] who found CH$_2$ radical species formed from CO and H$_2$ over Co and Ni catalysts.

Storch, Golumbic, and Anderson [10,29] have proposed a different mechanism for the Fischer-Tropsch reaction based on oxygenated intermediates, as shown in Figure I-2. They assumed that:

1) hydrogen is adsorbed as atoms on the surface of metal;
2) chemisorption of CO occurs on metal atoms with bonding similar to that in metal carbonyls;
3) adsorbed CO is partially hydrogenated according to equation 1.

While the overall scheme proposed describes details of chain growth not applicable to methanation, the initiation and the rate determining steps are important to the methane synthesis. For methanation, they proposed that the reaction chemistry may be modified according to
equation 7. The intermediate species (A) will form alcohol under certain circumstances and methane under others depending on the total pressure, the H$_2$/CO ratio, and the temperature.

For the second mechanism, the models of Bousquet et al. [4], Van Herwijner et al. [5], Fontaine [7], and Vannice [8] are very similar. They are represented in Figures I-3, I-4, I-6, and I-7, respectively. No details were given in reference [5], except that the surface reaction between hydrogen and the H$_2$CO complex was assumed to be the rate determining step. Fontaine [7] also chose this step to be an irreversible step, as well as the final methane-forming step as a second irreversible step. The relative rates of these two steps would then govern the surface concentration of the adsorbed H$_2$CO complex.

Vannice [8], encouraged by the large body of data that showed the ratio of 1:1 between hydrogen and CO on the surface, has postulated the mechanism as shown in Figure I-7. The model is very simple. It should be noted that the intermediate chemical species need not be defined (such as keto or enol) as long as a CO molecule and a H$_2$ molecule occupy the same surface site. Vannice also pointed out that a rate equation can be derived from the model proposed using the appropriate choice of y values, where y is the number of H atoms participating in the rate determining step.

Finally, there is an attempt to explain the mechanism of the reaction based on nonuniformity of the
surface. Boudart [35] proposed a more complicated model, involving the assumption of surface heterogeneity. This model involves two irreversible steps, which account for the difficulty in observing surface HCOH species under the reaction conditions. However, the final derived rate was similar to one of the simpler models.

Oxygenated theories have been widely studied. However, the postulated HCOH species has not been substantiated by spectroscopic evidence, while there is various infrared evidence supporting the formation of methylene radicals [34]. However, some investigators [36,37] have found H-O, C-O and C-H bonds on the surface of catalysts. The only spectroscopic evidence of a formate species was found in a study by Dalla Betta and co-workers [36] who found a carbonyl stretching band at $2043 \text{ cm}^{-1}$ for Ru/Al$_2$O$_3$ at 523 K. They also identified adsorbed formate species and adsorbed water. Therefore, due to the absence of strong evidence in favor of oxygenated intermediates, a number of investigators have revived the carbide theory. Surface H was observed by mass spectroscopy [31,95]. Similarly, infrared spectroscopy and Mossbauer spectroscopy have shown the dissociation of CO to form metal carbide [38,39,40,44].

Using mass spectroscopy, Joyner, et al. [38] and Barber, et al. [39] observed that CO was dissociated on polycrystalline Ni even at moderate temperatures. Similarly, Dalmon and Martin [40], using magnetic
measurements, have found Ni$_3$C on the surface of Ni supported on silica. They have found that this species reacts readily to form methane when heated in a hydrogen atmosphere. Iron carbide was also detected by Raupp and Delgass [41,42,43] using Mossbauer spectroscopy and their proposed mechanism based upon carbide formation is shown in Figure I-8.

Rabo and co-workers [44] have observed that CO will dissociate on Ni, Co, and Ru to form both metal carbide and graphite, and disproportionate to produce CO$_2$. They found two types of carbon deposits, graphite, which is inactive, and carbide, which is readily hydrogenated to methane. Using a CO and O$_2$ pulse method, they observed that C and CO coexist on the surface, except on Pd where the adsorption of CO is nonassociative. This work was similar to the finding by Wentreck et al. [45] who observed that the surface carbon formed through the dissociation of CO is more active toward hydrogen than the chemisorbed, but nondisassociated CO. However, there is no proof regarding the relative activities. Rabo and co-workers proposed the plausible mechanism shown in Figure I-9 for Co, Ru, and Ni. The choice between equation 2 and 3 depends on the reactivities of the metal-oxygen species toward H$_2$ and CO, respectively. Since in most cases, the metal-oxygen is more reactive to H$_2$, the production of H$_2$O dominates. The result from these experiments have indicated that the envisioned surface carbon route is probably not the only reaction path to hydrocarbon synthesis. The efficient conversion of mixed
\[
\begin{align*}
\text{CO} & \rightarrow \text{Ni}_4\text{CO}_{\text{ADS}} \quad \text{(1)} \\
\text{Ni}_4\text{CO}_{\text{ADS}} & \leftrightarrow \text{Ni}_3\text{C}_s + \text{NiO}_{\text{ADS}} \quad \text{(2)} \\
\text{Ni}_3\text{C}_s + \text{NiO}_{\text{ADS}} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{(3)}
\end{align*}
\]

Figure I-8. Mechanism Proposed by Dalmon and Martin [40].

\[
\begin{align*}
2\text{M (Ni, Co, Ru)} + \text{CO} & \rightarrow \text{M-C} + \text{M-O} \quad \text{(1)} \\
\text{M-O} + \text{H}_2 & \rightarrow \text{M} + \text{H}_2\text{O} \quad \text{(2)} \\
\text{M-O} + \text{CO} & \rightarrow \text{M}=\text{CO}_2 \quad \text{(3)} \\
\text{M-C} + 2\text{H}_2 & \rightarrow \text{M} + \text{CH}_4 \quad \text{(4)}
\end{align*}
\]

Figure I-9. Mechanism Proposed by Robo et al. [44].

\[
\begin{align*}
\text{CO} + \text{S} & \leftrightarrow \text{CO}_s \quad \text{(1)} \\
\text{CO}_s + \text{S} & \leftrightarrow \text{C}_s + \text{O}_s \quad \text{(2)} \\
\text{H}_2 + 2\text{S} & \leftrightarrow 2\text{H}_s \quad \text{(3)} \\
\text{C}_s + \text{H}_s & \leftrightarrow \text{CH}_s + \text{S} \quad \text{(4)} \\
\text{CH}_s + \text{H}_s & \leftrightarrow \text{CH}_2s + \text{S} \quad \text{(5)} \\
\text{CH}_2s + \text{H}_s & \leftrightarrow \text{CH}_3s + \text{S} \quad \text{(6)} \\
\text{CH}_2s + \text{H}_2 & \rightarrow \text{CH}_4 + \text{S} \quad \text{RDS (6')} \\
\text{CH}_3s + \text{H}_s & \rightarrow \text{CH}_4 + \text{S} \quad \text{RDS (7)}
\end{align*}
\]

Figure I-10. Mechanism Proposed by Ekerdt and Bell [48].
overlayers consisting of both surface carbon and non-
dissociated CO to hydrocarbons suggested that the
chemisorbed but nondissociated CO is also converted to
hydrocarbons. The efficiency of the latter route is,
however, much lower than the first route.

Several studies have been undertaken by infrared
spectroscopy to observe hydrogenation of CO. Dalla Betta
and Shelef [36] and King [46] have observed that the primary
species present on Ru/Al$_2$O$_3$ catalyst is chemisorbed CO.
Hydrocarbons and formate species were also found but have
been ruled out as adsorbed products which are active toward
the reaction. Similar works [46, 47] on silica-supported Ru
catalysts have also pointed out the abundance of adsorbed
CO.

Ekerdt and Bell, using infrared spectroscopy with CO
and hydrocarbons adsorbed on the surface of silica-supported
Ru catalysts, have found that the formation of relatively
high yields of C$_2$ and C$_3$ products is favored as the
temperature and the H$_2$/CO ratio decrease and as the partial
pressure of CO increases. When the reaction is run in the
absence of CO after the chemisorption of CO, the production
rates are found to be equal to or even exceed the rates
observed under steady-state conditions. This result
indicates the possibility of CO dissociation on the surface
of the catalyst. Ekerdt and Bell have also posed a
plausible mechanism as shown in Figure I-10. The sequence
is nearly identical to that proposed by Wagner [49] to
explain the formation of methane from carbon dissolved in iron. Reactions 6' and 7 can be considered as the rate limiting steps. However, based on equation 6' as the RDS, the kinetics are much more closely related to experimental data.

4. Bimetallic Catalysts

In spite of numerous works on metal loaded catalysts for the methanation reaction, few have investigated metal alloys. This can be partially attributed to the lack of understanding of the structure of alloys. It has been found by various investigators [50-52, 41-43] that the nature of metal loaded catalysts is altered significantly when a second metal is added. The effect can either enhance or retard the activity of the original catalyst.

Sinfelt [52] found that the addition of Cu to Ru supported silica reduces the activity of the catalyst, causing a decline in the turnover number of ethane hydrogenolysis even though the dispersion has increased. He was also able to determine that Cu atoms were totally immiscible with Ru in the bulk. Elliott and Lunsford [53] have found similar results with their studies of Ru-Ni, Ru-Cu, and Ni clusters in Y-zeolite. The addition of Ru to Cu supported zeolites decreases the activity. However, the addition of Ru to Ni clusters enhanced and stabilize the activity of the supported Ni catalysts. Furthermore, they found Ru clusters located in the large cavity of the zeolites in Ru/zeolites and Ni clusters located on the
exterior of the zeolites. However, the bimetallic clusters were found to be very small and distributed evenly throughout the structure of the support.

In a parallel study of Fe-Ni catalysts, Delgass and Raupp [41,42,43] found that an equimolar mixture of Ni and Fe supported on silica prevented the formation of carbide on the catalyst surface when the hydrogenation of CO was carried out at 523 K.

One of the biggest obstacles in the investigation of alloy catalysts is finding the proper method to characterize the catalysts. This is especially true in the case of determining the size distribution of the alloy clusters. Soma-Noto and Sachtler [87] found that even though both Pd and Ag adsorb CO readily, only Pd in PdAg alloys adsorb CO and that the structure of adsorbed CO depends heavily upon the neighboring atoms. Similarly, it has been found that the changes in the adsorption and catalytic properties of alloy surfaces are frequently not proportional to bulk composition, and this strongly suggests that there are significant differences between the bulk and the surface composition. Therefore, various physical techniques that are available for single metal catalyst are greatly handicapped in their usefulness.

B. OBJECTIVES

Ru and Fe are the two most reactive metals for the methanation reaction within the Group VIII metals. Due to the cost of a noble metal such as Ru or Pt, a number of
investigators have made attempts to alter the properties of these catalysts with the addition of a second metal to form a bimetal. Hence economic factors dictate the formulation of these bimetallic catalysts with a possible sacrifice in catalytic properties. One might reasonably expect an active Fe-Ru bimetallic catalyst which might also meet the economic conditions.

This research involves an attempt to determine the kinetic parameters and reaction mechanism as well as to define the surface characteristics of Ru loaded Y-Zeolite and Fe-Ru bimetallics loaded on Y-Zeolite. The work involves fundamental studies of surface structures using chemisorption with H₂ and CO, infrared spectroscopy, and ESCA. Kinetic studies and an isotopic dilution experiment have also yielded information on the nature of this system.

The purpose of this study was to determine the effects of the addition of Fe to Ru so that the value of the system as a catalyst could be assessed. This effect could be best illustrated in term of kinetic parameters as well as the surface properties of the catalysts. In this thesis, we have achieved some of the objectives as mentioned; however, the work does not cover all circumstances and, therefore, more research should be undertaken on this system.
II-EXPERIMENTAL

A. MATERIALS

The stock Ru catalyst was prepared by ion exchange of Ru complex, [Ru(NH₃)₆]Cl₂, with Na-Y Zeolite (Linde LZ-Y52) in distilled water. A small amount of ascorbic acid was added to minimize the oxidation of Ru. The ion exchange was performed under a helium atmosphere at 313 K with constant stirring. The process required two steps in order to assure quantitative uptake of Ru. Half of the total amount of Ru complex was mixed with Y-Zeolite for 12 hours followed by filtration, then exchange with the other half of Ru complex for another 12 hours. The catalyst was then washed with distilled water followed by methanol to remove moisture. The catalyst was dried at 323 K for 24 hours. The final analysis of this stock catalyst yielded 1.8% Ru by weight.

The Fe-Ru catalysts were prepared by impregnation of Fe onto the stock Ru-Y Zeolite. A solution of Fe complex was prepared from Fe(NO₃)₃·9H₂O. The Fe solution and Ru catalyst were mixed to obtain various compositions and were then dried at 373 K for 18 hours. The final compositions of the catalysts were:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ru</th>
<th>% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>C</td>
<td>1.8</td>
<td>3.7</td>
</tr>
<tr>
<td>D</td>
<td>1.8</td>
<td>5.9</td>
</tr>
</tbody>
</table>
All catalysts used for the reaction studies were pelletized, ground, and sieved to 20/40 mesh except for catalysts used for diffusional effect studies. Samples used in ESCA and infrared studies were in the non-pelletized form.

The following chemicals were used in this research:

\[
\begin{align*}
[Ru(NH_3)_6]Cl_2 & \quad \text{lot # 051981} \quad \text{Alfa Products} \\
Fe(NO_3)_3.9H_2O & \quad \text{lot # 37795} \quad \text{J.T. Baker Chemical} \\
Ascorbic Acid & \quad \text{lot # 56184} \quad \text{General Biochemical} \\
Na-Y Zeolite & \quad \text{lot # 9680770015-19} \quad \text{Union Carbide Corp.} \\
^{13}CO & \quad \text{lot # 625-G} \quad \text{MSD Isotopes} \\
\text{Deuterium} & \quad \text{lot # 2382-F} \quad \text{MSD Isotopes} \\
\text{Hydrogen} & \quad \text{C.P} \quad \text{Matheson} \\
\text{Carbon Monoxide} & \quad \text{C.P.} \quad \text{Matheson} \\
\text{Helium} & \quad \text{Zero} \quad \text{Big 3 Industries} \\
\text{Nitrogen} & \quad \text{Zero} \quad \text{Big 3 Industries}
\end{align*}
\]

Zero helium and nitrogen were used in the gas chromatograph as carrier gases. Prior to reaction, hydrogen was passed over Pd/Al_2O_3 at 773 K to react trace amounts of oxygen followed by a dehydrated 5A Molecular Sieve (Linde) trap thermostatted with liquid nitrogen to remove moisture. Carbon monoxide was passed through a molecular sieve trap with an acetone/dry ice bath to remove carbonyls and water. Similarly, helium used in the reactor system was passed through a molecular sieve trap with liquid nitrogen.
B. APPARATUS

1. Recirculation Reactor System

The reactor system shown in Figure II-1 was used for kinetic measurements. The system consisted of a batch recirculation reactor made of Pyrex glass with greased high vacuum stopcocks (S1 thru S20). The high vacuum system consisted of a 2" Varian diffusion pump which was liquid nitrogen trapped, a Varian Ionization/Thermocouple gauge, and a rotary mechanical pump. Pressures below $10^{-5}$ torr could be obtained routinely.

The reactants were stored in storage bulbs B1 thru B3. They were admitted into the recirculation reactor thru stopcock S1. With stopcock S2 closed the system pressure could be monitored with a tension diaphragm MKS Baratron type 221 A pressure gauge.

Under operating conditions, stopcocks S1 and S3 would be closed. The reactants were pumped through the mixing volume, reactor, and back again. Three-way stopcocks S4 and S5 could be set to connect volume V1 for pulse experiments. The volume for V1 as determined by mercury displacement was 1.95 cc. Three-way stopcocks S6 and S7 could be set to bypass the reactor. Trap T1 could be used with liquid nitrogen to remove the condensible compounds during the reduction step or could be used with an acetone/dry ice trap to remove water during the reaction in order to minimize the water-gas-shift reaction. The total volume of the recirculation reactor was 580 cc.
Figure II-1. Recirculation Reactor System and Chemisorption Apparatus
The reactor could be removed from the main recirculation reactor system through ground glass joints J1 and J2. Stopcock S8 could be used to close off the reactor to prevent the contamination of the catalyst when the reactor was removed from the system. The catalyst was packed between two glass wool plugs in a 12 mm OD Pyrex glass tube. A thermocouple well inside the catalyst bed allowed measurement of the temperature during the reaction. The temperature of the reactor was controlled with an Omega Model 151 temperature controller using a simple electric furnace. The temperature of a reactor could be controlled within +/- 1 K.

The recirculation pump consisted of a glass cylinder with an iron implanted glass piston. The piston could be moved back and forth via alternating magnetic fields which were provided by two solenoids surrounding the cylinder. The pump displacement was approximately 15 cc per second.

2. Chemisorption Apparatus

The adsorption isotherms were measured with a conventional Pyrex glass volumetric adsorption system employing greased high vacuum stopcocks. The diagram is included in Figure II-1 with the recirculation reactor system. This system consisted of known standard volumes V1, V2, and manifold. The pressure of the system could be monitored by either a high range pressure gauge, P3, for 0.0 to 1000.0 torr, or a low range pressure gauge, P2, for 0.00 to 100.00 torr. Both of the pressure gauges were tension
diaphragm MKS Baratron type 221 A Series gauges. The reactor could be connected to the chemisorption apparatus through ground glass joint J3. The temperature of the reactor was maintained by an electric furnace similar to the one previously described.

Various gases were stored in bulbs B4 thru B6. The system was pumped by the same diffusion pump/mechanical pump system previously described in the recirculation reactor system. A pressure of $10^{-5}$ torr could be obtained routinely.

3. Gas Chromatograph

A Carle Series-S Analytical Gas Chromatograph (AGC) 111-H was used in the analysis of the reactants and products in all the recirculation reaction experiments. Five columns were used in conjunction with three multifunction gas switching valves. The gas sample was analyzed by a thermistor detector. Hydrogen was separated from the sample thru a Hydrogen Transfer System (HTS) which consisted of a thin palladium tube heated to 773 K. Only hydrogen could diffuse through this metal tubing which escaped into a nitrogen carrier gas that swept the opposite side of the tube. One side of the thermistor detector monitored the nitrogen sweep while the other side monitored the helium carrier gas.

The column/valve arrangement is shown in Figure II-2, and a typical analytical sequence is presented in Table II-1. The column descriptions are presented in Table II-2.
Figure II-2. Column/Valve Arrangement for GC.

Table II-1. Typical Analytical Sequence for GC.
COLUMN LENGTH       PACKING

1A  17'  28% Bis(EE)A+4.7% Squalane+2% Carbowax 1560 on Chromosorb PAW, 80/100 mesh
1C  12"  28% Bis(EE)A+4.7% Squalane+2% Carbowax 1560 on Chromosorb PAW, 80/100 mesh
1B  18"  1% Tetraethylene Glycol Dimethyl Ether on Porasil C, 80/100 mesh
2    4'  Porapak N, 80/100 mesh
3    6'  Molecular Sieve 13X, 80/100 mesh

Table II-2. Column description

GAS CHROMATOGRAPH CONDITIONS

<table>
<thead>
<tr>
<th>Helium Flow Rate</th>
<th>61 ml/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Flow Rate</td>
<td>70 ml/min.</td>
</tr>
<tr>
<td>Column Temperature</td>
<td>348 K</td>
</tr>
<tr>
<td>HTS Temperature</td>
<td>793 K</td>
</tr>
<tr>
<td>Bridge Setting</td>
<td>6</td>
</tr>
<tr>
<td>Cycle Time</td>
<td>23 minutes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VALVE SEQUENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event</td>
</tr>
<tr>
<td>Time(min.)</td>
</tr>
<tr>
<td>Valve</td>
</tr>
<tr>
<td>Position</td>
</tr>
</tbody>
</table>

Table II-3. Programed valve sequences and AGC conditions
All valve switching was automatic.

Each column used was optimum for separating certain components. Columns 1A, 1B, and 1C were primarily intended for hydrocarbon separations. Columns 2 and 3 performed separations of H₂, O₂, CH₄, CO. In a typical analysis shown in Table II-1, valve V1 was used initially to inject the sample, and separations were made on columns 1A, 1B, and 1C through 1-pentene. After this analysis the columns were backflushed and valve V2 injected another identical sample on column 2 in series with column 3 and the HTS. Hydrogen was separated at column 3 and then transferred into the nitrogen carrier gas at the HTS and finally, proceeded to the detector TCD2. Before hydrogen was detected, column 3 was bypassed and CO₂, ethylene, and ethane were sent to the detector TCD1 from column 2. Column 2 was immediately backflushed to vent and column 3 again connected to detector TCD1, then O₂, N₂, CH₄, and CO were separated as they left column 3.

The output from the AGC was sent to a Hewlett-Packard 3390A integrator for analysis. The programmed AGC parameters and conditions are listed in Table II-3. The integrator parameters are listed in Table II-4 which included the relative molar responses (RMR) of various gases. The first column is the value of peak area/pressure in torr as calibrated by our standard mixtures. These values represent average values over a number of standard mixture sample. The actual response factors varied slightly
### INTEGRATOR PARAMETERS

- **Attenuation**: 2
- **Peak Width**: 0.04
- **Threshold**: 1
- **Area Reject**: 50

### RELATIVE MOLAR RESPONSE (RMR)

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>AREA/TORR x 10^5</th>
<th>( \frac{RMR_i}{RMR_{CO}} )</th>
<th>( \frac{RMR_i}{RMR_{CO}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>0.386</td>
<td>1.60</td>
<td>1.54</td>
</tr>
<tr>
<td>Propylene</td>
<td>0.379</td>
<td>1.57</td>
<td>1.50</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.438</td>
<td>1.81</td>
<td>1.95</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.480</td>
<td>2.00</td>
<td>2.02</td>
</tr>
<tr>
<td>Butene-1</td>
<td>0.504</td>
<td>2.08</td>
<td>1.93</td>
</tr>
<tr>
<td>Transbutene-2</td>
<td>0.487</td>
<td>2.01</td>
<td>2.02</td>
</tr>
<tr>
<td>1,3 Butadiene</td>
<td>0.461</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>Isopentane</td>
<td>0.619</td>
<td>2.56</td>
<td>2.40</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.643</td>
<td>2.66</td>
<td>2.50</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.292</td>
<td>1.21</td>
<td>1.14</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.306</td>
<td>1.26</td>
<td>1.14</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.324</td>
<td>1.34</td>
<td>1.22</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.095</td>
<td>0.39</td>
<td>-</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.242</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table II-4. Integrator Parameters. All RMR's were reported with a helium carrier gas except for \( H_2 \) which was detected in \( N_2 \).
as the chromatograph was recalibrated. Column two is the ratio of the RMR of each species to that of CO, and the last column is the value reported by Darry and Rosie [24]. Our values correspond closely to the published values. A typical chromatogram and its analysis are shown in Figure II-3.

4. ESCA

ESCA spectra were kindly taken by Dr. Jeffrey Donner at the Department of Chemistry at LSU. Samples were prepared from catalyst powder and pressed into a small disk. They were treated in flowing hydrogen for 12-15 hours at 773 K and cooled to room temperature before the spectra were taken. These treatments were accomplished inside the ESCA sampling chamber.

The ESCA spectrometer was a Perkin Elmer Physical Electronics Division (PHI) Model 548 ESCA/Auger system equipped with a PHI model 2100 sample introduction system with the optional PHI model 02-120 hot/cold specimen transport probe and a PHI model 32-030 Neutralizer for the minimization and elimination of sample charge. The ESCA/Auger system was interfaced to a Tracor Northern model TN-1505 signal averager allowing data to be collected digitally. The data was then transferred directly to a Perkin Elmer Interdata Division model 8/32 computer for analysis. The data could be processed to correct for background, high binding energy, side peak tailing, and line shape variation between Gaussian and Lorentzian. The result
Figure II-3. Typical Chromatogram and its Analysis.
was then plotted on a Tektronic model 4662 digital plotter.

5. Infrared Cell

A removable infrared cell was used in these experiments. It was made from a 7/8" by 3/8" rectangular Pyrex glass with a high vacuum stopcock. A picture of the cell is shown in Figure II-4. The catalyst wafer was held in place by a stainless steel holder 2 1/2" long and 5/8" wide, which could be slid from the bottom of the cell to the windows. The cell windows were made of NaCl and were 7/8" by 1 1/2". They were mounted perpendicular to the catalyst holder to allow the maximum infrared transmission.

The cell could be connected to the main recirculation reactor similar to the reactor previously described. Only the bottom part of the cell was immersed in the electric heater. The cell could be evacuated to $10^{-6}$ torr under dynamic vacuum. The stopcock could be closed off and the reactor removed for infrared analysis, hence preventing the contamination of the catalyst wafer by the atmosphere.

6. Fourier Transform Infrared Spectrometer

All the infrared spectra were taken with an IBM Instruments IR/32 Fourier Transform Infrared Spectrometer (FTIR) equipped with a He-Ne laser. The FTIR spectrometer system consisted of an IBM CS/9000 micro-processor for data acquisition and data analysis, two 8" disk drives, and a liquid nitrogen cooled Mercury-Cadmium-Telluride detector.
Figure II-4. The Infrared Cell.
The spectrometer covered the mid-infrared range from 4800 to 400 cm\(^{-1}\) which allowed all of the frequencies of this region of infrared energy to be measured simultaneously. It utilized a scanning Michelson interferometer to create the interference pattern characteristic of the frequencies and intensities of light which were seen at the detector. Under normal circumstances, 200 to 600 scans of the sample were sufficient to obtain a reasonable signal to noise ratio. The resolution was set at 2 cm\(^{-1}\).

C. EXPERIMENTAL PROCEDURES

1. Standard Treatment Conditions

Prior to each kinetic and infrared experiment, catalyst samples were reduced at 773 K with 200 torr of hydrogen and 560 torr of helium in the recirculation reactor for 15 to 17 hours. A liquid nitrogen trap was used to trap all the condensible compounds. It was found that at 773 K one could obtain the highest metal dispersion on all Ru and Fe-Ru catalysts, hence establishing standard conditions for the reduction process. Furthermore, a minimum of 12 hours was required in all cases for the reduction process in order to maintain constant activity of the catalysts. The sample was then cooled to 573 K under the hydrogen/helium atmosphere before evacuation at this same temperature. The catalyst was allowed to degas at 573 K under dynamic vacuum for only one half hour to minimize the chance that metal particles could be reoxidized. After evacuation, the pressure above the sample was less than 10\(^{-5}\) torr. This
procedure was followed for each subsequent reaction. The standard condition for the kinetic studies is defined at 523 K reaction temperature with a reactant mixture of $H_2$ to CO of 3 to 1.

2. Chemisorption Experiments

The chemisorption experiments were performed in the adsorption apparatus previously described. Typically, 0.5 grams of catalyst were treated as described in the pretreatment section in the recirculation reactor system prior to the chemisorption. The dead volume of the sample container was determined first by a P-V expansion using high purity helium. The reactor was connected to the apparatus thru the ground glass joint J3 (see Figure II-1). The constant volume V1, manifold, and pressure gauge P2 (low range pressure gauge) were normally used for this calculation. With stopcocks S13, S15, S16, S17, S19 closed, we could account for the available volume. Helium was then admitted through S17. Once the pressure of the standard volume reached equilibrium, the pressure in this known volume was recorded. Then stopcock S13 was opened allowing helium to expand into the evacuated reactor. Once the pressure stabilized, a second pressure reading was recorded. From these two pressure readings, an initial and a final, and a known standard volume one could calculate the dead volume of the reactor. This procedure was repeated three to five times to arrive at an average dead volume. Typically, volumes could be determined to +/- 0.01 cc.
Once the dead volume was determined, the reactor was evacuated at room temperature. After one half hour a typical pressure of $10^{-5}$ torr was routinely obtained. Hydrogen chemisorption followed, after which the sample was degased at 573 K for one hour followed by carbon monoxide chemisorption.

Both hydrogen and carbon monoxide adsorption were carried out in a manner similar to the dead volume measurement where one starts with a known standard volume and a measured pressure. The adsorbate gases were allowed to expand from the standard volume with a known initial pressure into the reactor at a number of pressure increments, from a pressure of 80 torr to 300 torr. However the reactor was not evacuated between each step and the number of moles of adsorbate gas was carefully accounted for as pulses were added. With a known standard volume, the initial pressure of adsorbate gas in the reactor, and the final pressure of the the standard volume plus the dead volume, one could calculate the amount of gas adsorbed onto the catalyst surface at each final pressure reading.

Hydrogen adsorption on both Ru-Y Zeolite and Fe-Ru Y Zeolite approached equilibrium slowly at room temperature. The equilibrium isotherm of hydrogen adsorption at a higher temperature showed identical results. However, equilibrium was reached much faster. After 30 minutes at 373 K, further adsorption was negligible. A similar slow adsorption was also observed for CO chemisorption on all four catalysts.
Both types of chemisorption yielded a linear isotherm from 100 to 250 torr indicating a completely covered surface. The extrapolation from this linear isotherm to zero pressure yielded the monolayer coverage of adsorbate [64].

3. Recirculation Experiments

A reactor containing about 0.5 gram of catalyst was connected to the recirculation reactor system thru ground glass joints J1 and J2. With stopcocks S6 and S7 rotated to evacuate the reactor, the catalyst was evacuated at room temperature until a pressure of about 20 microns was reached. With stopcock S2 closed, hydrogen was allowed to enter from glass bulb B2 to the recirculation reactor thru S1. A typical reduction process used 250 torr of hydrogen and about 510 torr of helium. The temperature of the reactor was slowly increased to 773 K while the hydrogen-helium mixture was circulated through the reactor. Liquid nitrogen was used at trap T1 to remove water in the system and the catalyst reduced overnight prior to the reaction.

After reduction was complete, the catalyst was cooled to 573 K under the recirculating hydrogen-helium mixture, then the reactor was bypassed via S6 and S7. The liquid nitrogen trap was removed from T1, and once the trap was warmed, S2 was opened allowing the system to be evacuated. Once the recirculation reactor system was completely evacuated, the catalyst was evacuated. Pressures below $10^{-5}$ torr could be obtained after 30 minutes of evacuation.
After the evacuation was complete, the reactor temperature was lowered to the reaction conditions, and a dry ice/acetone bath was placed at trap T1. The reactor was then bypassed via S6 and S7. With S2 closed, the reactants were admitted thru S1 and the pressure was monitored with gauge P1. CO was usually admitted first followed by hydrogen to yield a given mixture of $\text{H}_2/\text{CO}$. Helium was then admitted thru S12, passing through molecular sieve T2 which was immersed in liquid nitrogen, and then through S1. The final pressure was about 760 torr. The mixture of reactants was diluted by helium to improve the heat transfer in the reactor and to minimize atmospheric contamination. The reactant mixture was then condensed with liquid nitrogen at trap T1 and at the mixing volume to help mix the reactants. Once trap T1 and the mixing volume thawed, stopcock S3 was closed and the pump was turned on. The reactants were allowed to further mix for at least 15 minutes. The reaction was started by reconnecting the reactor thru S6 and S7 to the recirculation reactor system.

Samples could be removed from the recirculation reactor system thru S8 for gas chromatographic analysis. For the case of deuterated reactions, the procedures were identically the same except deuterium was used in place of hydrogen.

4. Infrared Experiments

For the infrared experiments, the catalyst was ground to a very fine powder in a mortar, and 25 to 35
milligrams pressed into a thin wafer with a hydraulic press. The typical pressure was in the range of 20000 to 23000 psi. The size of a wafer was 1/2" in diameter. This wafer was translucent to the eye and allowed observation in the infrared region. The wafer was placed in the infrared cell as previously described. The catalyst was then subjected to the same pretreatment as presented for the chemisorption experiments. After this pretreatment, the pressure above the wafer was about $10^{-5}$ torr. The cell was then cooled to room temperature under dynamic vacuum, closed off, and removed from the recirculation reactor, after which a reference spectrum of the clean catalyst was taken. Samples of CO, H$_2$, O$_2$, and mixtures thereof could then be adsorbed onto the wafer as described below and a spectrum taken.

**a. Carbon Monoxide Infrared Spectra**

Samples for CO spectra were prepared by chemisorption of CO onto a freshly reduced catalyst wafer at 298 K or 373 K. A range of 30 microns to 50 torr of CO were introduced into the infrared cell for 20 minutes. The pressure of the system usually reached equilibrium after 10 to 15 minutes. The cell was then cooled to room temperature followed by evacuation at room temperature until the pressure above the catalyst was $10^{-5}$ torr. The cell was then closed off and taken to the infrared spectrometer for analysis. Similar experiments were also carried out for catalysts which had been pre-exposed to oxygen.
b. Infrared Spectra after Co-adsorption of CO with H\textsubscript{2} and CO with O\textsubscript{2}

Experiments were carried out for each catalyst where the sample was first exposed to 11 torr of CO at 373 K for 20 minutes followed by cooling and evacuation to 10\textsuperscript{-5} torr. After evacuation, 5 torr of H\textsubscript{2} were admitted to the cell and the sample temperature was adjusted to either 298 K or 373 K for 20 minutes followed by cooling and evacuation to 10\textsuperscript{-5} torr. The sample was then ready for infrared analysis.

Following the same idea, various samples were treated with a cycle of CO exposure followed by O\textsubscript{2} exposure and possibly with another CO exposure. All the chemisorption steps were carried out at 373 K. The initial CO exposure was typically in the range of 30 torr while later exposures were 5 torr.

c. Isotopic Dilution Experiments

Infrared experiments with mixtures of\textsuperscript{12}CO and \textsuperscript{13}CO were also carried out at 373 K in a manner identical to the previous experiments for CO spectra. A range of mixtures from 10\% \textsuperscript{12}CO to 90\% \textsuperscript{12}CO at a total pressure of 11 torr were chemisorbed at 373 K for 20 minutes, then cooled to room temperature and evacuated for 5 minutes prior to spectral analysis.

d. Methanation Reaction at 523 K

In a manner similar to previous infrared measurements, a catalyst wafer was also analyzed after being subjected to methanation reaction conditions which
duplicated conditions used for kinetic studies. A standard reaction was performed over the infrared ready wafer; after 1 hour of reaction, the reaction was stopped, the wafer was cooled and evacuated to $10^{-5}$ torr after which a spectrum was taken. The same experiment was also performed with $D_2$ replacing $H_2$. 
A. KINETIC MEASUREMENTS

1. Catalytic Aging

In order to understand the effect of catalytic aging on all four catalysts, runs were made on three consecutive days with a reduction step every day for each catalyst. Typical results for catalyst A and catalyst D are shown in Figures III-1 through III-6. These figures represent the result of the methanation reaction at 523 K. The partial pressures of both the reactants, CO and H₂, and the product methane are plotted as functions of time.

Hence it is apparent that when the catalysts were treated under standard conditions, as described in the pretreatment section, the catalysts retained constant activity for several days. As demonstrated by Figures III-1 through III-6, repetition of the reduction process produces little effect on the long term activity indicating that the metal particles are stable and that irreversible carbon poisoning does not occur.

Therefore, all catalysts used for kinetic measurements were activated in the same manner before the reaction. The data were taken from runs over a period of 10 to 12 days where the catalysts were repeatedly reactivated overnight.
Figure III-1. Partial Pressure of CO during the Methanation Reaction at 523 K over Catalyst A.
Figure III-2. Partial Pressure of H$_2$ during the Methanation Reaction at 523 K over Catalyst A.
Figure III-3. Partial Pressure of CH₄ during the Methanation Reaction at 523 K over Catalyst A.
Figure III-4. Partial Pressure of CO during the Methanation Reaction at 523 K over Catalyst D.
Figure III-5. Partial Pressure of H₂ during the Methanation Reaction at 523 K over Catalyst D.
Figure III-6. Partial Pressure of CH₄ during the Methanation Reaction at 523 K over Catalyst D.
2. Diffusional Effects

To demonstrate that diffusional effects were not influencing the kinetics of the methanation reaction, two catalysts of different particle size were prepared. The experiments consisted of reaction under standard conditions described in the previous chapter using 0.5 gm of the usual 20/40 mesh size catalyst and another run with 0.5 gm of 40/60 mesh size catalyst under the same conditions. A typical result is shown in Figure III-7 where the partial pressures of both methane and CO are plotted as functions of time. The results indicate that there is no mass transfer resistance in the methanation reaction because the conversions are essentially the same on both particle sizes.

3. Methanation Kinetics

Figures III-8 through III-14 represent the conversion of CO for typical runs on catalysts A, B, C, and D. The open symbols in these 7 plots represent the actual experimental values as defined by the following equation:

$$f_{CO}^j = \frac{\sum n_{ci} p_i^j}{p_{CO}^j + \sum n_{ci} p_j^j}$$
Figure III-7. The Comparison of the Methanation Reaction at 523 K for two Catalyst mesh sizes.
Figure III-8. The Comparison of CO Fractional Conversion over Catalyst A at Various Temperatures.
Figure III-9. The Comparison of CO Fractional Conversion at 523 K over Catalyst A at Various H\textsubscript{2}:CO Mixtures.
Figure III-10. The Comparison of CO Fractional Conversion at 533 K over Catalyst A at Various H₂:CO Mixtures.

CO FRACTIONAL CONVERSION

- □: H₂:CO = 3:1 at 533 K 5-12-83
- ○: H₂:CO = 3:2 at 533 K 5-13-83
- ▲: H₂:CO = 2:1 at 533 K 5-13-83

CATALYST TYPE: 1.8% RU

- CO RATE CONSTANT: 0.001200
- H₂ RATE CONSTANT: 0.022200
- CO ORDER: -0.60
- H₂ ORDER: 1.20
Figure III-11. The Comparison of the Methanation Reaction over Catalyst B at Various Temperatures.
Figure III-12. The Comparison of CO Fractional Conversion at 523 K over Catalyst B at Various H₂:CO Mixtures.
Figure III-13. The Comparison of the Methanation Reaction over Catalyst C at Various Temperatures.
Figure III-14. The Comparison of the Methanation Reaction over Catalyst D at Various Temperatures.
where

\[ f_{co}^j = \text{fractional conversion with respect to CO at } j^{\text{th}} \text{ sampling time} \]

\[ n_{ci} \]

\[ P_{ij}^j = \text{partial pressure of species } i \text{ at } j^{\text{th}} \text{ sampling time} \]

\[ P_{co}^j = \text{partial pressure of CO at } j^{\text{th}} \text{ sampling time} \]

The solid lines in all these figures represent the results of the numerical solution to two first order differential equations resulting from writing the rates of reaction for the two reactants as described below:

\[
\frac{dP_{CO}}{dt} = -k_{CO} (P_{CO})^X (P_{H_2})^Y \tag{2}
\]

\[
\frac{dP_{H_2}}{dt} = -k_{H_2} (P_{CO})^X (P_{H_2})^Y \tag{3}
\]

where:

\[ P_{CO} = \text{partial pressure of CO} \]

\[ P_{H_2} = \text{partial pressure of } H_2 \]

\[ k_{CO} = \text{rate constant with respect to CO} \]

\[ k_{H_2} = \text{rate constant with respect to } H_2 \]

\[ X = \text{CO reaction order} \]

\[ Y = \text{H}_2 \text{ reaction order} \]

These two differential equations represent the rate of disappearance of the two reactants with respect to time. The techniques used in arriving at the numerical solutions
involve the initial guesses of the two rate constants, $k_{\text{CO}}$ and $k_{\text{H}_2}$, and the two reaction orders, $X$ and $Y$. Once the initial guesses were made, a Runge-Kutta numerical integration routine was used to solve these two coupled differential equations. The solutions which were obtained from this integration were compared with the actual partial pressures measured during the course of the experimental run. The sum of the square of the errors was then obtained, and used as criteria in a pattern search program which found the best values for $k_{\text{CO}}$, $k_{\text{H}_2}$, $X$, and $Y$.

The pattern search method was put forward by Hooke and Jeeves [30]. This method consists of an initial guess with a given "cost". The procedure involved numbers of "exploratory moves" where each variable was perturbed by a given step size and the cost was recalculated per each change. These costs were then compared to arrive at the least cost. Once the least "cost" was obtained, the variables were changed to accommodate this new cost, thus establishing a new set of variables. The analysis of the results as obtained by the numerical solution to the two rate equations followed this same criteria where the variables in this analysis were the initial guesses of the rate constants and the reaction order and the cost was the total error previously described. The pattern search routine involved the change of these variables one at a time followed by the Runge-Kutta routine to solve for the partial pressures. These partial pressures were corrected for
changes in volume due to the sampling procedure which was amounted to less than 1.5% of the total volume. The pattern search program also contains an acceleration routine to double the step sizes when the error value decreases very rapidly, and reduce the step sizes when the total error cost decreases slowly. The initial step size for the rate constants was 0.01 and the initial step size for the reaction orders was 0.1. The total number of step size reductions was limited to 10. There were also a number of constraints in the program. The values of the reaction orders were limited between -4.0 and 4.0, and the values of the rate constants could not be zero or negative. The routine was terminated when the optimal error, in this case the minimum error was reached. Finally a small perturbation near the optimal point followed by the same pattern search was used to check for a global minimum as opposed to a local minimum.

Once the values of \( k_{CO} \), \( k_{H_2} \), \( X \), and \( Y \) were obtained the value of the fractional conversion of CO could be calculated as:

\[
f_{CO}(t) = \frac{P_{CO}(t)}{P_{CO \text{ int}}}
\]  

where:

\[
f_{CO}(t) = \text{fractional conversion of CO}
\]

\[
P_{CO}(t) = \text{partial pressure of CO from the numerical solution}
\]

\[
P_{CO \text{ int}} = \text{initial partial pressure of CO}
\]
Table III-1 summarizes the results of the kinetic analysis. The effects of both the H₂ concentration and CO concentration are quite obvious. In the case of catalyst A, an increase in H₂ partial pressure accelerates the rate of reaction while an increase in the CO partial pressure decelerates the rate of reaction. This observation is true over the entire temperature ranges studied. The same qualitative results were also observed in all bimetallic catalysts.

4. Activation Energy

The effect of temperature on the reaction rate is clearly demonstrated in Figure III-8 for catalyst A, in Figure III-11 for catalyst B, in Figure III-13 for catalyst C, and in Figure III-14 for catalyst D. The values of $k_{CO}$ were calculated at various temperatures by the pattern search program but using fixed reaction orders as calculated at 523 K. The results are presented in Arrhenius plots in Figures III-15 thru III-18. Hence, activation energies were obtained from these plots for the temperature range of 503 K to 543 K, and are included in Table III-1.

5. The Reaction of CO with D₂

The reaction of CO with D₂ was also observed at 523 K with a 1:3 ratio of CO to D₂. The results are presented in Figures III-19 to III-21 for catalyst B, C, and D. The substitution of H₂ by D₂ produced little effect on the overall rate of disappearance of CO, but it increased the
Table III-I. Kinetics of Methanation Reaction over Ru and Fe-Ru Bimetallic Catalyst

\[ r = -\text{A}e^{E/RT}(P_{CO})^{x}(P_{H2})^{y} \]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature Range</th>
<th>X</th>
<th>Y</th>
<th>Activation Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8% Ru</td>
<td>513-533</td>
<td>-0.6</td>
<td>1.2</td>
<td>84</td>
</tr>
<tr>
<td>1.8% Ru 1.2% Fe</td>
<td>503-543</td>
<td>-0.6</td>
<td>0.9</td>
<td>58</td>
</tr>
<tr>
<td>1.8% Ru 3.7% Fe</td>
<td>503-543</td>
<td>-0.6</td>
<td>0.8</td>
<td>41</td>
</tr>
<tr>
<td>1.8% Ru 5.9% Fe</td>
<td>503-543</td>
<td>-0.6</td>
<td>1.1</td>
<td>60</td>
</tr>
</tbody>
</table>
Figure III-15. Arrhenius Plot for Catalyst A.
Figure III-16. Arrhenius Plot for Catalyst B.
Figure III-17. Arrhenius Plot for Catalyst C.
Figure III-18. Arrhenius Plot for Catalyst D.
Figure III-19. The Comparison of the Methanation Reaction at 523 K using \( \text{H}_2/\text{CO} \) Mixture and \( \text{D}_2/\text{CO} \) Mixture over Catalyst B.
Figure III-20. The Comparison of the Methanation Reaction at 523 K using H₂/CO Mixture and D₂/CO Mixture over Catalyst C.
Figure III-21. The Comparison of the Methanation Reaction at 523 K using H₂/CO Mixture and D₂/CO Mixture over Catalyst D.
rate of production of methane. The inverse isotope effect observed in this work is similar to the result obtained by Bell and co-workers [31]. This result indicates that the rate of reaction is not limited by the rate of H₂ dissociation.

6. Product Distribution

The product distribution reported is defined at 20% conversion of the limiting reactant, CO. However, the product distribution is essentially constant with conversion. The values are tabulated in Table III-2 for all four catalysts. The product distributions are grouped into 5 categories: methane, 2-carbon species, 3-carbon species, 4 or more carbon species, and carbon dioxide. The graphic representation is shown in Figure III-22. The product distribution based on the Schultz-Flory theory is shown in Figure III-23 where relative molar concentration is plotted against the carbon number.

B. SURFACE ANALYSIS

1. ESCA Spectra

Samples for ESCA spectra were reduced in flowing H₂ at the rate of 60 cc/hr at 773 K for 15 hours, followed by cooling to 573 K and evacuation at this temperature for 1 hour. All the treatments were performed inside the sample prechamber to prevent atmospheric contamination. A pressure of 10⁻⁵ torr was normally obtained before insertion into the main chamber. The samples were then allowed to cool to room temperature under dynamic vacuum before the spectra were
<table>
<thead>
<tr>
<th>Ru/Fe</th>
<th>CH₄</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄⁺</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8/0.0</td>
<td>81.0</td>
<td>9.8</td>
<td>5.9</td>
<td>2.5</td>
<td>0.8</td>
</tr>
<tr>
<td>1.8/1.2</td>
<td>72.4</td>
<td>10.7</td>
<td>9.5</td>
<td>5.6</td>
<td>1.8</td>
</tr>
<tr>
<td>1.8/3.7</td>
<td>57.0</td>
<td>11.6</td>
<td>11.7</td>
<td>6.0</td>
<td>14.5</td>
</tr>
<tr>
<td>1.8/5.9</td>
<td>51.8</td>
<td>9.8</td>
<td>12.0</td>
<td>5.5</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Table III-2. Product Distribution at 523 K for H₂:CO = 3:1 at 20% Conversion of CO
Figure III-22. Product Distribution at 20% Conversion during the Methanation Reaction at 573 K.
Figure III-23. $C_n$ versus Carbon Number during the Methanation Reaction at 523 K over Catalyst A.
taken. All binding energies are referenced to Si 2p at
102.54 eV. Table III-3 summarizes the results of the ESCA
studies. An example of ESCA raw data is also shown in
Figure III-24 for catalyst A. The interpretation is rather
straight forward. The value of 279.4 eV corresponds to Ru
3d_{5/2} and is identified as Ru^0. The peak at 709.3 eV is
identified as Fe^{2+} and corresponds to Fe 2p_{3/2}. Finally the
705 eV peak together with the 719.0 eV peak are identified
as Fe^0, corresponding to Fe 2p_{3/2} and Fe 2p_{7/2}
respectively.

2. Chemisorption Results

H_2 adsorption on both Ru-Y Zeolite and Fe-Ru Y-
Zeolite approach equilibrium slowly at room temperature.
After 30 minutes under hydrogen pressure at 298 K, further
adsorption was negligible. The equilibrium isotherm of H_2
adsorption at higher temperature showed an identical
monolayer coverage as at room temperature except that the
equilibrium was attained in a shorter period of time. A
similar slow adsorption was also observed for CO on
all four catalysts. Both types of chemisorption
isotherms yield a linear isotherm from 100 to 250 torr
indicating a completely covered surface. The extrapolation
from this linear isotherm to zero pressure yields the
monolayer coverage of the adsorbate [64]. Based on this
information we arrive at the number of the active sites,
both H_2 active and CO active, assuming one H atom per site
and one CO per site. The dispersion is obtained by dividing
<table>
<thead>
<tr>
<th>Metal XPS Peak</th>
<th>CATALYST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Ru $3d_{5/2}$</td>
<td>279.4</td>
</tr>
<tr>
<td>Fe $2p_{3/2}$</td>
<td>709.3</td>
</tr>
<tr>
<td>Fe $2p_{7/2}$</td>
<td>721.9</td>
</tr>
</tbody>
</table>

TABLE III-3. Metal Binding Energies for Each Catalyst after Reduction in eV Relative to Si $2p = 102.54$ eV.
Figure III-24. ESCA Spectrum of Ru $3d_{5/2}$ of Freshly Reduced Catalyst A.
the total number of active sites by the total number of (Fe + Ru) atoms. A typical chemisorption of H\textsubscript{2} and CO on Fe-Ru catalyst, after reduction at 773 K and evacuation at 573 K, is given in Figure III-25. A table showing the dispersion and capacity of each catalyst is shown in Table III-4.

3. Infrared Spectra

a. Effect of Coverage

All of the catalyst wafers were treated under the same standard conditions previously described prior to infrared experiments. The pretreatment conditions consisted of a reduction step with H\textsubscript{2} and He mixture at 773 K for at least 12 hours followed by degasing at 573 K for 30 minutes. The samples were then cooled to room temperature under dynamic vacuum.

In order to understand the relationship between the surface coverage of CO and the corresponding infrared band frequency, an infrared experiment was designed such that a reduced catalyst sample was exposed to CO at various pressures. The experiment was carried out in an IR cell where the sample was exposed to CO at 373 K for 20 minutes, followed by cooling both the sample and the CO gas phase to 298 K before evacuating at this temperature for 5 minutes. The spectrum of the sample was then taken at 298 K. The infrared spectra of catalyst A, which has been exposed to CO at 373 K, as a function of coverage are shown in Figures III-26 and III-27. At the lower pressure range of 36 microns there is only one broad peak at 1960 cm\textsuperscript{-1}. Upon
Figure III-25. H₂ Chemisorption Isotherm at 373 K of Freshly Reduced Catalyst C.
<table>
<thead>
<tr>
<th>Ru/Fe</th>
<th>Total Hydrogen Active Sites ($10^{-6}$ mole/gm)</th>
<th>Dispersion (H$_2$ Chem.)</th>
<th>Total CO Active Sites ($10^{-6}$ mole/gm)</th>
<th>Metal Crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8/0.0</td>
<td>106</td>
<td>0.59</td>
<td>256</td>
<td>15</td>
</tr>
<tr>
<td>1.8/1.2</td>
<td>83</td>
<td>0.22</td>
<td>215</td>
<td>-</td>
</tr>
<tr>
<td>1.8/3.7</td>
<td>25</td>
<td>0.03</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>1.8/5.9</td>
<td>22</td>
<td>0.02</td>
<td>75</td>
<td>-</td>
</tr>
</tbody>
</table>

Table III-4. Hydrogen and Carbon Monoxide Chemisorption Data at 373 K.
Figure III-26. Infrared Spectra in the CO Absorption Region at 373 K on a Reduced Catalyst A Sample at (A) 36 millitorr, (B) 140 millitorr, and (C) 11 torr.
Figure III-27. Infrared Spectra in the CO Absorption Region at 373 K on a Reduced Catalyst A Sample at (A) 11 torr, (B) 30 torr, and (C) 50 torr.
increasing the pressure there are more peaks to be found at 2000, 2046, 2080, 2102, 2130, and 2157 cm\(^{-1}\). Every peak remains unchanged when the pressure is increased from 11 torr to 50 torr with the exception of the peaks at 2007 and 2041 cm\(^{-1}\). The peak at 2041 cm\(^{-1}\) shifts to 2046 cm\(^{-1}\) while the peak at 2007 cm\(^{-1}\) shifts to 2010 cm\(^{-1}\).

b. Effect of Temperature

A parallel experiment was also carried out at 298 K to compare the effects of adsorption temperature as well as the exposure duration on the frequencies of the CO bands on catalyst A. In this case the sample was exposed to 28 torr of CO at 298 K. The spectra of the sample were taken at various time intervals at 298 K under CO atmosphere where the background was corrected for CO gas phase. The infrared spectra of the sample as a function of time are shown in Figure III-28. Spectrum A represents the adsorption after 1 hour. The spectrum is dominated by a very broad peak around 2040 cm\(^{-1}\) with a shoulder at 2107 cm\(^{-1}\) and smaller peaks at 2156 and 2169 cm\(^{-1}\). As the time of adsorption increases, the broad adsorption around 2040 cm\(^{-1}\) produces a number of resolved and distinct peaks at 2025, 2041, 2051, and 2074 cm\(^{-1}\) (see spectrum D in Figure III-28). It also becomes evident that peaks at 2108 and 2169 cm\(^{-1}\) grow and decrease together indicating that they are dependent upon each other. After 54 hours of adsorption, there are only two sharp peaks at 2041 and 2080 cm\(^{-1}\) with shoulders at 2024, 2048, and 2108 cm\(^{-1}\). There are also
Figure III-28. Infrared Spectra in the CO Absorption Region at 298 K on Reduced Catalyst A: (A) after 1 hour, (B) after 9 hours, (C) after 23 hours, (D) after 54 hours, and (E) after evacuation at 298 K for 18 hours.
weaker bands at 2126, 2135, 2157, and 2169 cm$^{-1}$. Upon evacuation at room temperature for 18 hours the spectrum E resembles the initial adsorption at 1 hour. The peaks at 2180 and 2108 cm$^{-1}$ have decreased drastically and only appear as shoulders. A similar observation also holds true for the bands at 2126, 2135, 2157, and 2169 cm$^{-1}$ after 18 hours of evacuation. There is only one shift observed, the shift of the band at 2073 cm$^{-1}$ at 1 hour adsorption to 2080 cm$^{-1}$ after 54 hours.

A similar experiment was performed on a freshly reduced catalyst A wafer which was initially exposed to 30 torr CO at 298 K for 20 minutes; then the sample was heated to 373 K and held for 20 minutes. The sample was then cooled to room temperature before it was evacuated for 5 minutes. The spectrum was recorded at 298 K. This spectrum is then compared to the adsorption of CO at 373 K under the same conditions in Figure III-29. The sample at 298 K produces similar spectra as observed previously, however upon increasing the temperature to 373 K the spectrum becomes resolved and produces a distinct number of bands. There are sharp bands at 2043 and 2082 cm$^{-1}$ with a shoulder at 2101 cm$^{-1}$ and three smaller peaks at 2126, 2157, and 2168 cm$^{-1}$. There are numbers of similarities between spectrum B and spectrum C, however the band at 2168 cm$^{-1}$ is absent in the case where the sample was exposed to CO at 373 K.
Figure III-29. Infrared Spectra in the CO Absorption Region on Reduced Catalyst A. (A) 30 torr CO at 298 K after 20 min., (B) then heated to 373 K for 20 min., then evacuated at 298 K for 5 min., and (C) 30 torr CO at 373 K after 20 min.
c. Effect of Oxygen

The effect of oxygen on adsorbed CO on catalyst A and the adsorption of CO on an oxidized catalyst A are shown in Figure III-30. All the spectra were taken at 298 K. The spectrum A represents a reduced sample which was initially exposed to 30 torr of CO at 373 K for 20 minutes and then evacuated at 298 K for 5 minutes. Spectrum B shows the effect of the exposure of the sample to 5 torr of O\textsubscript{2} at 373 K and spectrum C represents the readsorption of CO on the sample at 5 torr and 373 K for 20 minutes. Finally the spectrum D represents the sample which has been previously reduced and then was exposed to 10 torr of O\textsubscript{2} at 373 K for 10 minutes, then degased at 373 K for 10 minutes. The sample was later exposed to 30 torr of CO under the same conditions as spectrum A.

The exposure of adsorbed CO to low pressure oxygen at 373 K produces a drastic reduction in the two very sharp peaks at 2046 and 2081 cm\textsuperscript{-1}. This partially oxidized catalyst gives rise to only one strong band at 2082 cm\textsuperscript{-1} with shoulders at 2101 and 2068 cm\textsuperscript{-1}. There are also three weaker bands at 1981, 2016, and 2157 cm\textsuperscript{-1}. Upon the reintroduction of 5 torr of CO at 373 K for 20 minutes, there is only a small restoration of the band at 2077 cm\textsuperscript{-1}. The adsorption of CO on an oxidized catalyst produces only one sharp band at 2171 cm\textsuperscript{-1} and two very broad bands at 2137 and 1980 cm\textsuperscript{-1}. Interestingly the locations of the major bands were not effected by the exposure to oxygen at 373 K,
Figure III-30. Infrared Spectra in the CO Absorption Region on Reduced Catalyst A. (A) 30 torr CO at 373 K after 20 min., (B) then exposed to O₂ at 373 K, (C) reexposed to 5 torr CO at 373 K, (D) 30 torr CO at 373 K on an oxidized sample for 20 min.
however the major peak at 2082 shifted to 2077 cm$^{-1}$ upon the re-exposure of the sample to 5 torr of CO. This spectrum (spectrum C) is very similar to the adsorption of CO on the oxidized sample (spectrum D).

In order to identify the higher frequency bands correctly, a number of CO chemisorption experiments were carried out on catalyst A samples that had received different oxygen pretreatments. Figures III-31 and III-32 represent the studies on CO adsorption at 373 K on catalyst A samples that have been treated with oxygen at various temperatures and conditions. Figure III-31 shows the effect of the duration of CO adsorption at 373 K on the sample that has been exposed to 10 torr of oxygen at 373 K for 10 minutes followed by evacuation at the same temperature for 10 minutes. The spectrum after one hour is very similar to spectrum D in Figure III-30. There is only one sharp band at 2072 cm$^{-1}$ and numbers of smaller bands at 2001, 2021, 2102, 2137, and 2157 cm$^{-1}$. After 8 hours (see spectrum B) there are at least two sharp bands at 2081 and 2050 cm$^{-1}$ and a shoulder at 2101 cm$^{-1}$. There is evidence that the major peak at 2072 cm$^{-1}$ found after 1 hour has shifted to 2081 cm$^{-1}$ while the less intensive bands at 2021 and 2001 cm$^{-1}$ after one hour shift to 2006 and 1980 cm$^{-1}$. Spectrum C shows the effect of evacuation of the sample after 18 hours. The major band at 2081 cm$^{-1}$ has decreased though this spectrum still resembles the initial adsorption after one hour.
Figure III-31. Infrared Spectra in the CO Absorption Region on oxidized Catalyst A. (A) after 1 hour, (B) after 9 hours, and (C) after evacuation at 298 K for 18 hours.
Figure III-32. Infrared Spectra in the CO Absorption Region for: (A) CO adsorption on oxidized Catalyst A, (B) CO adsorption on oxidized Catalyst A which was evacuated at 573 K for 18 hours, and (C) CO adsorption on Catalyst A that was oxidized at 573 K.
Figure III-32 shows the effect of the pretreatment of the oxidized sample prior to the adsorption of CO at 373 K. Spectrum A is the same as spectrum C in Figure III-31. Spectrum B represents the CO adsorption on a sample that has been exposed to 5% O₂/He mixture at 373 K for 1 hour then evacuated at 573 K for 18 hours. Spectrum C represents 30 torr of CO at 373 K on 1.8% Ru that was exposed to 10 torr oxygen at 573 K for one hour then evacuated at 573 K for one hour. Spectra A and C give essentially the same shape, however the sizes of the peaks in spectrum C is much smaller due to the loss of transmission and possible sintering effect caused by oxygen. The interesting result is spectrum B which represents the oxidized sample that has been evacuated at an elevated temperature for 18 hours. The peaks found in this sample have the same characteristics as the ones found in CO adsorption on freshly reduced catalysts. All the major peaks at 2081, 2047, 2126, 2157, and 2168 cm⁻¹ are found in this sample as spectrum A in Figure III-27.

**d. Effect of Hydrogen**

Under similar conditions, a sample which was pre-exposed to 11 torr of CO at 373 K for 20 minutes then evacuated at room temperature for 5 minutes was subjected to 5 torr of H₂ at 298 K for 20 minutes (spectrum B in Figure III-33). In this case there was only a small effect on the sample, notably a small reduction in the band at 2080 cm⁻¹. However when the same sample was treated with 5 torr of H₂
Figure III-33. Infrared Spectra in the CO Absorption Region on Reduced Catalyst A. H₂ effect on adsorbed CO on Catalyst A at 373 K.
at 373 K for 20 minutes there was a large effect on the sharp bands at 2080 cm\(^{-1}\) and on a smaller band at 2030 cm\(^{-1}\). The overall effect on the sample was to produce one broad band around 2044 cm\(^{-1}\) and 2004 cm\(^{-1}\) (spectrum C). \(\text{H}_2\) also causes a small shift in the band at 2046 to 2044 cm\(^{-1}\), also the previous shoulder at 2007 becomes a more distinct band at 2004 cm\(^{-1}\).

e. CO Adsorption on Bimetallic Catalysts

Finally, all four catalysts were exposed to CO at 373 K and the spectra at 298 K are compared in Figure III-34. All four catalysts were subjected to the same reduction process previously mentioned. The spectra represent the adsorption of CO at 373 K for 20 minutes, which were cooled to room temperature before they were evacuated for 5 minutes. Samples A and B show similar bands; however the bands of catalyst B (spectrum B) show a drastic reduction in the amount of adsorbed CO. All the major peaks found in A are found in spectrum B with a slight shift in the band at 2046 cm\(^{-1}\) in A to 2043 cm\(^{-1}\) in B and a band at 2007 cm\(^{-1}\) in A to 2003 cm\(^{-1}\) in B. Spectra C and D are magnified 4 times in order to enhance the image. These two spectra are similar to each other but much different from the pure Ru and lightly loaded Fe-Ru catalyst. The major peak at 2080 cm\(^{-1}\) and small shoulders at 2102 and 2007 cm\(^{-1}\) are almost extinct in these catalysts. Both spectra C and D produce a broad band about 2040 cm\(^{-1}\) with a small shoulder at 2080 cm\(^{-1}\). Again, the only significant shift relative to spectra
Figure III-34. Infrared Spectra in the CO Absorption Region on Reduced Catalysts. 11 torr CO at 373 K on (A) Catalyst A, (B) Catalyst B, (C) Catalyst C, and (D) Catalyst D.
A occurs in the major peak at 2040 cm$^{-1}$ in A to 2043 cm$^{-1}$ in C and to 2040 cm$^{-1}$ in D.

f. Isotopic Dilution Experiments

Isotopic dilution experiments were carried out in a manner similar to the chemisorption of CO on catalysts A thru D. The sample wafer was reduced the same as those previously described. The CO adsorption was carried out at 373 K with a total CO pressure of 11 torr. The isotopic experiments involved the successive dilution of $^{12}$CO with $^{13}$CO. The exposure time was 20 minutes followed by cooling to room temperature before evacuation at this temperature for 5 minutes. The spectra were taken at 298 K similar to the rest of the infrared experiments.

It has already been clearly illustrated in Figures III-26 and III-27 that the frequency of CO adsorbed on the pure Ru catalyst increases due to the increasing dipole-dipole effect of adjacent CO molecules as a totally covered surface is achieved. On the contrary, bimetallic catalysts at a relative high pressure of 11 torr (see Figure III-34) exhibit only CO-Ru bands while CO-Fe bands were absent. In Voroshilov's studies [65], the adsorption of CO on ferric oxide of different reduction states gave rise to bands in the infrared region at 2180, 2070, 2020 cm$^{-1}$ for CO adsorbed on Fe$_2$O$_3$, FeO, and Fe, respectively. The CO bands due to various Fe oxidation states which were observed by Voroshilov et al. were not found in these experiments. However, the effect of the addition of Fe onto the stock Ru
Y-Zeolite is illustrated by the two major CO-Ru bands at 2080 and 2046 cm\(^{-1}\). The band at 2080 cm\(^{-1}\) decreases as the amount of Fe increases and the CO-Ru band at 2046 cm\(^{-1}\) shifts downward to 2040 cm\(^{-1}\) for catalyst D. The major effect of the addition of Fe to Ru catalyst is on the magnitude of CO adsorption. The addition of Fe produces a drastic reduction on CO uptake on the surface of the catalyst. Likewise the addition of Fe also reduces the magnitude of the band at 2080 cm\(^{-1}\). Another observation is that, even though the band at 2046 cm\(^{-1}\) shifts, the magnitude is quite small.

Isotopic dilution is found to be a very useful tool in the case of bimetallic catalysts. This technique is very important in identifying the various effects produced by alloying two different metals. The dilution of \(^{12}\)CO with \(^{13}\)CO often reveals information which is hidden by dipole-dipole interactions of the adsorbate. It is found by various investigators [58-61] that upon diluting \(^{12}\)CO with \(^{13}\)CO, they could gain information about the geometrical and electrical effects produced by alloying. Using this technique, the characteristic changes of the infrared spectra of adsorbed CO by the alloying effect of Ru with Fe is illustrated in Figures III-35 thru III-38. The effect of several isotopic mixtures for pure Ru and three other Fe-Ru catalysts on the medium frequency band of 2046 cm\(^{-1}\) are shown in Figure III-39. It is clear that the effect of Fe on the CO-Ru frequency is not as pronounced with pure \(^{12}\)CO
Figure III-35. Infrared Spectra in the CO Absorption Region for Isotopic Dilution on Reduced Catalyst A: (A) 100% $^{12}\text{CO}$, (B) 33% $^{12}\text{CO}$, and (C) 20% $^{12}\text{CO}$.
Figure III-36. Infrared Spectra in the CO Absorption Region for Isotopic Dilution on Reduced Catalyst B: (A) 100% $^{12}$CO and (B) 25% $^{12}$CO.
Figure III-37. Infrared Spectra in the CO Absorption Region for Isotopic Dilution on Reduced Catalyst C: (A) 80% $^{12}$CO and (B) 50% $^{12}$CO.
Figure III-38. Infrared Spectra in the CO Absorption Region for Isotopic Dilution on Reduced Catalyst D: (A) 70% $^{12}$CO and (B) 40% $^{12}$CO.
as it is with $^{13}\text{CO}$. The addition of $^{13}\text{CO}$ into $^{12}\text{CO}$ produces a strong effect, decreasing this medium frequency band. The extrapolation of this curve to pure $^{13}\text{CO}$ produces the singleton frequency for the $^{12}\text{CO}$-Ru band at $1993 \pm 5$ cm$^{-1}$. This singleton frequency is the frequency which would be obtained if all dipole-dipole interactions were removed. It is clearly demonstrated in Figure III-39 that the addition of Fe into the Ru catalyst produces no significant effect on the singleton frequency of CO on Ru. All the data for various isotopic dilution mixtures fall, within the experimental error, on the same path suggesting that, at least on the surface, Fe atoms do not participate in the Ru matrix. The overall effect clearly demonstrates that Fe produces neither a geometrical nor an electrical effect on the Ru atom.

g. Infrared Spectra After Methanation Reaction Conditions

In order to understand the mechanism of the methanation reaction, it is important to understand the nature of the adsorbed species on the catalyst surface. Therefore, a number of infrared spectra were taken for catalysts which had been exposed to methanation reaction conditions. The reaction was carried out under the same conditions as the kinetic studies where the catalyst wafer was reduced overnite at 773 K under H$_2$-helium mixture with a liquid nitrogen trap in line. The sample was cooled to 573 K before evacuation. The pressure above the wafer was about
Figure III-39. Isotopic Dilution Experiment.
10^{-5} \text{ torr} \text{ after 5 minutes of evacuation at this temperature. The temperature of the wafer was then lowered to the reaction condition at 523 \text{ K} \text{ before exposure to the reactant mixture. After one hour of reaction, the infrared cell was bypassed and was allowed to cool to room temperature before evacuating at this temperature for 5 minutes. The spectra were then taken at 298 \text{ K} \text{ and are shown in Figures III-40 thru III-43.}

Figure III-40 represents the spectra of catalyst A after one hour of reaction. There is one dominant peak around 2000 \text{ cm}^{-1} \text{ representing the linear adsorption of CO. There is an absence of the multiple CO adsorption at 2080 \text{ cm}^{-1} \text{ on the surface of the catalyst. The difference between the reacted catalyst wafer and the freshly reduced wafer exposed to CO is a small increase in the peak at 1643 \text{ cm}^{-1} \text{ and smaller peaks at 2870 and 2930 cm}^{-1}. The first peak at 1643 \text{ cm}^{-1} \text{ is probably the scissor vibration of the water molecule commonly found in the range of 1650-1600 \text{ cm}^{-1} [66]. The other two smaller peaks represents assymmetric C-H stretching vibrations for the CH}_2 \text{ group at 2930 cm}^{-1}, and symmetric C-H stretching vibrations for the CH}_3 \text{ group at 2870 cm}^{-1 [67].}

The infrared spectrum after the methanation reaction on catalyst B is shown in Figure III-41. The result is similar to the plain Ru catalyst. The CO linear adsorption is found at 2000 \text{ cm}^{-1}. There is a slight increase in the water band at 1640 \text{ cm}^{-1}. Similar to catalyst A, the
Figure III–40. Infrared Spectra in the CO Absorption Region for the Methanation Reaction at 523 K over Catalyst A after 1 hour.
Figure III-41. Infrared Spectra in the CO Absorption Region for the Methanation Reaction at 523 K over Catalyst B after 1 hour.
Figure III-42. Infrared Spectra in the CO Absorption Region for the Methanation Reaction at 523 K over Catalyst C after 1 hour.
Figure III-43. Infrared Spectra in the CO Absorption Region for the Methanation Reaction at 523 K over Catalyst D after 1 hour.
presence of the C-H vibrational bands at 2870 cm$^{-1}$ due to the \text{CH}_3 group, at 2924 cm$^{-1}$ due to \text{CH}_2 group, and a new band at 2964 cm$^{-1}$ due to the assymmetric \text{CH}_3 stretching [67] are apparent.

The catalyst C spectrum is shown in Figure III-42. The result is similar to the previous two catalysts with the exception of a small shift in the CO band from 2000 cm$^{-1}$ to 2005 cm$^{-1}$. The highest percentage Fe catalyst D produces similar results (see Figure III-43) with the exception of a large shift in the CO band from 2000 to 2021 cm$^{-1}$. This shift is also observed in the case of isotopic dilution experiments previously described. The transmission of this particular wafer reduced markedly after the reaction causing a loss in the detail of the infrared spectrum in the range of 3200 to 2500 cm$^{-1}$. Therefore the C-H peaks at 2900-2800 cm$^{-1}$ were not observed. However the presence of the water molecule on the surface was still detectable at 1643 cm$^{-1}$.

\textbf{h. Infrared Experiment with D$_2$}

In order to distinguish some of the infrared bands, a series of experiments with deuterium replacing hydrogen were performed. The same conditions used in the infrared experiments which were performed after the methanation reaction were employed except that D$_2$ was substituted for H$_2$. An example is shown in Figure III-44, which is a typical result observed on all four catalysts. The CO peak is found at the usual location indicating that D$_2$ produces no isotope effect on the adsorbed CO. There are new broad
Figure III-44. Infrared Spectra in the CO Absorption Region for the Methanation Reaction at 523 K with D₂/CO Mixture over Catalyst B after 1 hour.
peaks from 2780 to 2500 cm\(^{-1}\) with sharp peaks at 2760, 2730, and 2700 cm\(^{-1}\). These three peaks probably represent the oxygen-deuterium stretching vibration and correspond to the O-H peaks at 3745, 3737, and 3698 cm\(^{-1}\) [68]. The presence of an O-D bond indicates that even though steps were taken to minimize the water gas shift reaction, there is still significant water built up on the surface of the catalyst. This is to be expected since the source of water is the reaction on the surface.

i. CO and CO\(_2\) Chemisorption

In order to understand the nature of surface carbon, an experiment was carried out for which the surface of the catalyst was intentionally covered with carbon. This catalyst was later exposed to CO\(_2\). The sample was originally exposed to 50 torr of CO at 373 K for 30 minutes, then cooled to room temperature before evacuation at this temperature for 5 minutes. Figures III-45 and III-46 show various effects of treatments on the adsorbed CO on catalyst B. Figure III-45 shows an evolution of surface CO upon heating. Spectrum A shows the typical peaks previously described. Upon heating the sample to 523 K for 30 minutes, spectrum B was the result. The two sharp bands at 2080 and 2043 cm\(^{-1}\) disappeared giving rise to one broad band centered around 2000 cm\(^{-1}\). The most striking result is the appearance of a CO\(_2\) band at 2350 cm\(^{-1}\). This sharp band is most likely the result of the disproportionation reaction of surface CO.
Figure III-45. Infrared Spectra in the CO Absorption Region on Reduced Catalyst B:
(A) 50 torr at 373 K for 30 min., then (B) heated to 523 K for 30 min.
Figure III-46. Infrared Spectra in the CO Absorption Region on Reduced Catalyst B: (A) 50 torr at 523 K after 1 hour, (B) evacuated at 523 K for 10 hours, (C) after 100 torr CO\textsubscript{2} at 523 K for 1 hour.
A similar sample was heated at 523 K in 50 torr of CO for one hour. These conditions are generally favorable for the disproportionation of CO [69]. The spectrum taken at 298 K is shown in Figure III-46 curve A. Spectra B represents the sample after 10 hours of evacuation at 523 K. The spectrum shows a very broad band from 2100 to 1940 cm\(^{-1}\). This broad peak is probably due to residual, unreacted CO. This sample was then exposed to CO\(_2\) at 523 K for one hour. The result is shown in spectra C. The obvious result was the sharp rise in absorption intensity at 2000, 2040 and 2080 cm\(^{-1}\). These peaks are probably the result of the reverse disproportionation reaction, i.e.:

\[
\text{C(s) + CO}_2\text{(g) } \text{--->} \text{ 2 CO(s)}
\]
IV - DISCUSSION

A. INTERPRETATION OF CHEMISORPTION AND ESCA

One of the most important aspects of the Ru and Fe-Ru Zeolite is its degree of reduction. It is found that the hydrogen uptake and the activity of all four catalysts are strongly dependent on the temperature and the duration of the reduction process. Claussen and Good [96] have found using Mossbauer spectroscopy that \([\text{Ru(NH}_3\text{)}_5\text{N}_2]^2+\) exchanged with NaY can be completely reduced to the metallic state in flowing hydrogen at 673 K. Similarly Jacobs et al. [97] have determined that Ru on Y Zeolite from \(\text{Ru(NH}_3\text{)}_3^3+\) exchanged with NaY could be reduced to its metallic state at a temperature as low as 573 K. These observations are also confirmed by our chemisorption and ESCA results which indicate that Ru has been reduced to its metallic state. However the Fe-Ru bimetal is apparently difficult to reduce to its metallic state as evidenced by the ESCA analysis. From our ESCA results it appears that there are significant quantities of Fe\(^{2+}\) with traces of Fe\(^0\) after the reduction process. Furthermore, the chemisorption isotherms of both \(\text{H}_2\) and CO show a drastic reduction in gas uptake when Fe was added to the Ru catalyst. The addition of Fe to the catalyst A decreases not only the calculated overall dispersion but also the total adsorptive capacity of the catalysts with respect to both \(\text{H}_2\) and CO adsorption. The dispersion as calculated from \(\text{H}_2\) chemisorption decreases
from 0.59 with catalyst A to just under 0.02 for catalyst D. Similarly, the total $H_2$ active sites drops from $106 \times 10^{-6}$ mole/gm for catalyst A to $22 \times 10^{-6}$ mole/gm for catalyst D.

These phenomenon can be partially explained by a well known characteristic of the Fe particle. It has been observed that iron oxide must first form a large particle via sintering before a full reduction can be accomplished [70]. Raupp and Delgass [41] have shown the effect of drying conditions on the particle size growth. They found that small particles resulting from a vacuum-dried catalyst cannot be reduced (only about 15% Fe$^0$ is formed). However, large particles are completely reduced to zero valent Fe under similar conditions. Therefore, it is quite common to attempt to accelerate the reduction of highly dispersed metal catalysts by simply adding a second metal which is highly active to $H_2$ activation, e.g. Ru.

There are only small amounts of work done on the Fe-Ru system. Ru is known to form a solid solution with Fe [71,72] only when the Ru concentration is higher than 24.5 mole %, and the hexagonal close-pack (HCP) crystal structure is formed. In the concentration range of 24.5 to 4.5 mole % Ru, a two-phase region consisting of an Ru enriched HCP structure and an Fe enriched body-centered cubic (BCC) structure exists. When the concentration of Ru falls below 4.5 mole %, Ru is substituted into the BCC structure of the Fe lattice. Contrary to these guidelines for the bulk system, Delgass et al. [73], using Mossbauer to study the
surface structure of unsupported FeRu powder, found that Fe is enriched on the surface, forming iron oxide islands which partially cover the Fe-Ru alloy. In similar studies of a silica-supported FeRu system with less than 1 wt% Ru loading [74], the Mossbauer results of impregnated, calcined, and reduced FeRu samples show that Fe cannot be reduced to a zero valent state either with or without Ru. However when Ru was added to the catalyst, the degree of reduction decreased. It is apparent that the low degree of reduction which was observed by these investigators and by our investigation is due to both the presence of small particles and to the poor metallic interaction between Fe and Ru. Starting with Ru and adding Fe, as in our investigation, simply results in a conglomerate in which Ru blocks the formation of large iron oxide particles and thereby causes the Fe to be even more difficult to reduce. The reduction in the numbers of both H₂ and CO active sites observed in this work is consistent with the fact that iron oxides which have lower surface tensions than Ru will preferentially migrate to the surface of the bimetallic crystallite thereby preventing the adsorption of both H₂ and CO on Ru sites. Iron oxides do not adsorb H₂ or CO to appreciable extent.

B. INTERPRETATION OF INFRARED BANDS

Despite numerous works [75-80] done on CO adsorption on Ru, there are only a few agreements on the band assignments. In general, all researchers agree on the band assignment of the linear adsorption form, Ru-CO, and the
bridged form, Ru-CO-Ru. These two bands are generally found in the range of 2050-2000 cm\(^{-1}\) for linear adsorption and in the range 1950-1870 cm\(^{-1}\) for bridge adsorption. Dalla Betta [77] has assigned the band at 2039 cm\(^{-1}\) to linear adsorption for 5% Ru/alumina. Similarly, Bell [75] identified the band at 2040 cm\(^{-1}\) as a linear adsorption, while Brown [78] assigned the band at 2030 cm\(^{-1}\) in his work on the adsorption of CO on 6% Ru on silica as the linear form. This was followed by the work of Goodwin [79] who assigned the band at 2045 cm\(^{-1}\) to a linear CO adsorption on highly dispersed Ru particles on Y-Zeolite. The bridged form assignment is due to the work of Guerra and Schulman [80] who assign the broad band around 1910-1870 cm\(^{-1}\) to bridge type adsorption.

However, assignments for the higher frequency bands around 2080 cm\(^{-1}\) and around 2150 to 2100 cm\(^{-1}\) are not well known. All investigators [76-79,81-83] agree that these bands represent the symmetric vibration and asymmetrical vibration of multiple CO adsorption on a single Ru atom. However disagreement persists on the nature of the Ru atom itself. Dalla Betta's studies [77] which involve the dependence of the CO vibrational frequency as a function of the Ru crystallite size led him to speculate that the higher frequency bands represent multiple CO adsorption on a single Ru atom with a low coordination number. In contrast, Brown [78] assigns these same bands to CO adsorbed on an Ru atom perturbed by a nearby oxygen. Similarly, Bell [76] and
Goodwin [79] believe that these bands are associated with multiple adsorption of CO on a partially ionized Ru atom.

From this study, we found that the bridged form of adsorption occurs first at low CO pressures. A broad band of CO adsorption is observed around 1950 cm⁻¹ at 36 millitorr of CO pressure at 373 K (Spectrum A, Figure III-26). At higher pressures, the bands around 2000 to 2040 cm⁻¹ begin to appear corresponding to the linear adsorption previously identified [76-79]. Comparing these spectra to CO adsorption at room temperature (spectrum A, Figure III-28) leads to the speculation that this broad adsorption around 2040 cm⁻¹ represents the distribution of linearly adsorbed CO on sites differing in their activation energy levels. This broad band reflects the surface heterogeneity of the Ru catalyst. Further adsorption at pressure higher than 10 torr at 373 K produces sharp bands at 2080, 2101, 2130, and 2157 cm⁻¹. These bands are sensitive to the duration of evacuation at room temperature and the original spectrum at lower pressures can be obtained after 18 hours of evacuation. This leads us to the conclusion that these bands must represent the multiple adsorption of CO on single Ru atoms whereby the adsorption is not as strong as a linear form, hence the adsorption is reversible under vacuum. Furthermore the bands at 2080 and 2130 cm⁻¹ are also sensitive to H₂ and to O₂ (Figures III-30 and III-33).

The effect of O₂ treatments have revealed numbers of interesting observations. When an Ru sample was subjected
to $O_2$ at 373 K for 10 minutes followed by CO adsorption, we found one sharp peak at 2071 cm$^{-1}$ with numerous smaller peaks at 2001, 2012, 2102, and 2137 cm$^{-1}$ (Figure III-32 spectrum A). However, when a similar sample was subjected to a severe $O_2$ treatment at 573 K for 1 hour followed by CO adsorption, there are only two peaks left at 2075 and 2130 cm$^{-1}$. The catalyst in the first case probably still retains some Ru crystallites in their metallic states, but in the latter case, all surface Ru atoms have been converted to Ru oxides, probably RuO$_2$. Hence the peaks at 2075 and 2130 cm$^{-1}$ are probably due to CO adsorption on ruthenium oxides. Similarly, when a sample was oxidized at 373 K for a short time, then evacuated at 573 K for 18 hours followed by CO adsorption at 373 K, the spectrum (spectrum B, Figure III-32) is very similar to CO adsorption on a reduced catalyst under the same conditions (Figure III-27). This result indicates that the process of oxidation occurs only on the very top layer of the Ru crystallite and is probably in the form of chemisorbed oxygen which can be removed by a simple evacuation at elevated temperatures. Furthermore, the peaks at 2080, 2101, 2137, and 2157 cm$^{-1}$ in Figure III-26 must represent multiple CO adsorption on Ru metal that has chemical properties which resembles Ru$^{2+}$. This is strongly supported by ESCA results of the Ru catalyst which indicates that Ru is in its metallic state after the reduction. Also highly dispersed Ru is found to be stable once reduced.
The effect of the exposure time on the oxidized Ru sample reveals numbers of interesting phenomenon. After 8 hours of CO adsorption on an oxidized sample, the spectrum we obtained (Figure III-31) reproduces the spectrum of CO adsorption on a reduced sample. Two sharp peaks are observed in both cases with a slight shift in the band at 2046 cm\(^{-1}\) for the case of the reduced sample to 2050 cm\(^{-1}\) for the oxidized sample. This band probably represents linear CO adsorption with a nearby oxygen. This behavior is probably the result of surface reduction by CO which occurs as:

\[
\text{CO}_s + \text{O}_s \rightarrow \text{CO}_2,
\]

because excess CO\(_2\) was also detected.

By comparing the spectrum of CO adsorption at 298 K with the adsorption at 373 K, it become obvious that the band found at 2080 and 2137 cm\(^{-1}\) in both cases are functions of time and temperature. These bands did not appear strongly until 54 hours of exposure in the case of the 298 K adsorption but were well defined in the case of 373 K adsorption after only 20 minutes. These temperature dependencies together with the evolution of CO\(_2\) point to the possibility of another surface reaction, probably a disproportionation reaction, such that CO reacts on certain Ru atoms in the absence of both oxygen and H\(_2\) to produce carbon and carbon dioxide and leaves partially ionized Ru atoms. This is strongly supported by the ESCA spectrum of the reduced Ru catalyst where it is found that Ru exists
only in its zero valent state. The other set of infrared bands at 2101 and 2157 cm\(^{-1}\) probably represents multiple CO adsorption on similar Ru atoms but with different activation energy levels. The infrared locations of these four bands are similar to the bands found in various carbonyl ligands in Ru complex such as Ru(CO)\(_4\)Cl\(_2\) [83], Ru(CO)\(_4\)Br\(_2\) [83], and Ru(CO)\(_4\)I\(_2\) [84].

The nature of adsorbed CO as represented by the four bands at 2080, 2101, 2137 and 2157 cm\(^{-1}\) is more revealing when the spectra of all four of catalysts are compared (Figure III-34). The addition of Fe to Ru has effectively changed the availability of Ru for CO adsorption. At the lowest Fe concentration on catalyst B, one observes a drastic reduction in the adsorption capacity of Ru. Thus, the results from both ESCA and chemisorption studies can be interpreted to mean that the surface is partially covered by iron oxides, therefore reducing the capacity of the catalyst for CO adsorption. At higher Fe concentrations, the effect on the high frequency bands is very obvious. The catalyst surface is now composed of two distinct metal regions. One is rich in Ru and the other is rich in iron oxides. The structure can be imagined as Ru islands which are surrounded by iron oxides. We would expect the encroachment of Fe on the Ru islands to affect mainly the multiple CO adsorption sites, because multiple CO adsorption is thought to occur on Ru atoms with low coordination number, that is, Ru atoms at the edges of corners as previously speculated by Dalla Betta
Thus, upon the encroachment of nearby iron oxides, the edge Ru atoms are deprived of multiple CO adsorption due to blockage by the iron oxide. Therefore Ru sites are only available for linear adsorption of CO. This is consistent with the observation that catalyst D has a spectrum at high CO pressure similar to catalyst A at 140 millitorr CO pressure where the surface is populated by linearly adsorbed CO.

C. INTERPRETATION OF ISOTOPIC DILUTION EXPERIMENT

The isotopic dilution method involves the infrared studies of isotopic mixtures of $^{12}\text{CO}$ and $^{13}\text{CO}$. The experiment is based on the fact that the dipole-dipole coupling is largest between dipoles with equal singleton frequencies [85]. So, upon substituting an isotopic substrate which has a substantially different singleton frequency, one can eliminate the coupling effect and hence the actual singleton frequency can be obtained. Therefore, upon the dilution of $^{12}\text{CO}$ with $^{13}\text{CO}$, one can obtain a singleton frequency for CO/Ru. This singleton frequency value is then used as a basis for the comparison of various catalysts. The singleton frequencies of Ru and Fe-Ru bimetallic catalysts have been compared and the results can be used to identify the effects of alloying; namely, geometrical effects and electronic effects [87,98,99]. The geometrical effect is an effect which involves the relative position of the adsorbent atoms and usually arises with the decrease of contiguous identical atoms. A catalytic
reaction which requires a minimum conglomeration of similar atoms will be severely affected by geometrical effects. On the other hand, alloying alters the electronic structure of the metals due to the adjacent foreign atoms. The use of the isotopic dilution method is found to be very useful in distinguishing these two phenomena [100-104]. Upon diluting $^{12}\text{CO}$ with $^{13}\text{CO}$ one slowly eliminates the dipole-dipole effect. At infinite dilution (as $^{13}\text{CO}$ approaches 100%) the singleton frequency of $^{12}\text{CO}/\text{Ru}$ is obtained. These values of $^{12}\text{CO}/\text{Ru}$ singleton frequencies are compared using the following criteria:

a. If the effect of Fe on the adsorption band of CO on Ru is entirely electrical, where the only effect is on the bond strength between the CO molecule and the Ru metal, then the plot of frequency versus dilution of $^{12}\text{CO}$ will be parallel for all four catalysts.

b. If the effect of Fe on the adsorbed CO/Ru is purely geometrical then Fe atoms would act like $^{13}\text{CO}$, increasing the distance between similar atoms and reducing the dipole-dipole coupling. Therefore, at infinite dilution of $^{12}\text{CO}$, a pure geometrical effect will yield identical singleton frequencies for all four catalysts.

c. If both effects are realized then an intermediate result would be observed.
d. If the additional Fe atoms produce neither the geometrical effect nor the electrical effect then all the curves of frequencies as a function of dilution will coincide.

It is obvious from Figure III-34 that the addition of Fe into stock Ru catalyst produces a drastic effect on the CO/Ru bands at 2080, 2101, 2137 and 2157 cm\(^{-1}\) attributable to multiple adsorption sites. This alloying effect is due to the reduction of Ru active sites at the edges and corners of the Ru crystallite, greatly reducing the amount of multiple adsorption of CO. The overall effect of alloying could best be demonstrated in Figure III-39 which represents the results of the isotopic dilution experiments. The results at various isotopic dilutions on all four catalysts produce a single path for all four types of catalysts. It is clearly demonstrated that by alloying Ru with Fe, there is no geometrical or electronic effect on the primary CO/Ru band. It is also important to point out the absence of any effect on the bridged adsorption around 1950-1870 cm\(^{-1}\). The additional Fe affects only the overall adsorption but it does not effect the relative intensity between linear adsorption and the bridged adsorption. This effect is normally observed in other alloying system such as PdAg [86] and NiCu [87]. In the PdAg alloys system, Sachtler and co-workers [86] observed a drastic reduction in the relative intensity between linear CO/Pd and bridged CO/Pd when Ag was added. This result indicates that both Pd
and Ag enter into a solid solution on the surface of the alloy crystallite. In contrast to this finding, we find that Fe and Ru do not form solid solutions on the surface even though the bulk may have the properties of an Fe-Ru alloy.

This postulate is clearly supported by the value of the singleton frequency for $^{12}$CO/Ru. This singleton value is the same for both pure Ru and Fe-Ru bimetallic catalysts. The relationship between the CO/Ru frequency and the percentage of the $^{12}$CO isotope produces only one path indicating there is an absence of metallic interaction between Ru and Fe. Based on this evidence as well as the results from the chemisorption experiments, we believe that there are segregated islands of Ru and iron oxides on the surface and there is no evidence of alloying on the surface. The surface is probably comprised of islands of Ru surrounded by a sea of iron oxide. These islands of Ru most likely interfere with the nucleation of iron oxides, thus preventing the critical iron oxide crystallite size to be reached so it could be reduced.

D. KINETICS AND REACTION SCHEMES

The kinetics of the methanation reaction over Ru and Fe-Ru bimetallic reported in Table III-1 have been correlated according the the following expression:

$$r = -Ae^{-E/RT}(P_{CO})^{X}(P_{H_2})^{Y}$$
The results obtained for the pure Ru loaded Y-Zeolite are similar to the results reported by other investigators [17,18,88] and summarized in Table II-2. There is a general agreement among all these investigators concerning the order with respect to the partial pressure of \( H_2 \). Though there is a general consenses that the reaction order with respect to \( CO \) is negative, the magnitude of the order is significantly different. This work yields the power with respect to \( CO \) partial pressure as -0.6 which is in good agreement with the works of Vannice [17] and of Ekerdt and Bell [88].

Though there are numerous works on Ru catalysts, there are very few works on Ru bimetallic catalysts, and almost none for the Fe-Ru system. Unsupported FeRu catalysts were studied by Delgass and co-workers [73,89,90] for the \( CO + H_2 \) reaction. Delgass and co-workers reported drastic changes in both the selectivity as well as activity by varying the composition of Fe and Ru in unsupported Fe-Ru bimetallic catalysts. They reported a significant drop in activity for the initial introduction of Fe in Ru [89] but a further increase in Fe restored partially the original activity of the pure Ru catalyst. This phenomenon was demonstrated to be a result in a change in particle size. Similarly, the addition of Fe to Ru changed the selectivity of the bimetallic catalysts and this change was shown to be due to surface Fe enrichment in FeRu bimetallic. Unfortunately, there was no report on the reaction orders for \( H_2 \) and \( CO \).
We have found that the activity of the bimetallic decreased significantly with the initial introduction of Fe (catalyst B) as presented both in the chemisorption experiments and in the turnover numbers. The turnover number, based on the rate of methane production and from the number of H\(_2\) active sites, decreased from 1.15 x 10\(^{-3}\) molecule/site-sec for catalyst A to 0.78 x 10\(^{-3}\) molecule/site-sec for catalyst B. Upon increasing the concentration of Fe, the overall activities of the catalysts was partially restored. The selectivity was also influenced by the Fe composition. Methane was the predominant product for the case of pure Ru, however when Fe was added, the long chain hydrocarbons became the dominating products. The most significant change in product distribution was found in carbon dioxide which grew from under 1% for pure Ru to well over 20% for catalyst D.

The selectivity of these catalyst could be explained in terms of the availability of the H\(_2\) active sites and CO active sites which were clearly demonstrated in the chemisorption experiments as well as in ESCA results. The addition of Fe into the Ru catalyst reduced the number of both H\(_2\) and carbon active sites. This is also supported by a drop in the reaction order with respect to H\(_2\) partial pressure. The addition of Fe did not appreciably effect the order with respect to CO indicating that CO was strongly held on the surface of the catalyst. In the case of pure Ru, there was an abundant supply of surface H\(_2\) due to the
highly reducible nature of Ru particles. This reservoir of \( \text{H}_2 \) is readily available for the hydrogenation of surface carbon. Therefore, surface carbon is most likely to be converted to methane before the chain propagation could start, hence resulting in a large production of methane. However, the addition of Fe into Ru Y-Zeolite reduced the number of \( \text{H}_2 \) active sites due to its inability to be completely reduced. Therefore, there is an insufficient amount of surface \( \text{H}_2 \) to convert the surface carbon to methane, hence, chain propagation is more likely to occur before chain termination of 1-carbon species. This explains the change in the selectivity and in the product distribution from mostly methane in the case of pure Ru to longer chain hydrocarbons in the case of the Fe-Ru bimetallic.

The high level of carbon dioxide production in Fe-Ru bimetallic catalysts can be explained by the nature of the decomposition of the CO molecule on Ru and on Fe particles. CO dissociates readily on Fe to produce surface carbide probably in the form of \( \text{FeC}_3 \) but this dissociation occurs to a lesser extent on Ru [69]. Low and Bell [69] noted that the dissociation of CO on a supported Ru catalyst most likely occurred on the support itself because Ru does not form a carbide with carbon. The addition of Fe to Ru catalyst in this study reduced adsorbed \( \text{H}_2 \), and this \( \text{H}_2 \) deficient surface probably encouraged the decomposition of surface CO. There is also infrared evidence that adsorbed
CO dissociated into C and CO\textsubscript{2} much easier upon heating from 373 K to 523 K especially in the case of Fe containing catalysts. This phenomenon is clearly demonstrated with the adsorption cycle of CO-evacuation-CO\textsubscript{2} as shown in Figure III-46. It is quite clear that there is surface carbon present on the catalyst due to the disproportionation reaction and this carbon could be converted to CO when exposed to CO\textsubscript{2}. The other source of CO\textsubscript{2} production was probably from the water-gas-shift reaction where

\[ \text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2 \]

Even though special care was taken to trap all the water in the system with a dry ice/acetone bath a considerable amount of CO\textsubscript{2} was produced. This reaction could not be prevented totally because of the parallel reaction process on surface Fe oxide where water was produced on the surface which later reacted with adsorbed CO.

**E. MECHANISM OF THE METHANATION REACTION**

There is evidence both in this work and in others [88,36,91] that CO is first adsorbed in a molecular state after which dissociation follows. The infrared studies from this work have indicated that the surface of both Ru and Fe-Ru bimetallic catalysts exhibited a nearly saturated CO coverage during the course of the reaction. Similarly, when a sample was initially exposed to CO at 373 K followed by heating to 523 K, there was an appreciable amount of CO\textsubscript{2} evolved from the adsorbed CO. Furthermore, the chemisorption experiments showed that the ratio of adsorbed
CO to adsorbed H atoms was larger than unity. This is a good indication that the surface is saturated with CO molecules. Furthermore, infrared spectra showed evidence of CO multiple adsorption on the metal particles. The process accompanying the formation of CO$_2$ is believed to occur by the following steps [92]:

\[
\begin{align*}
\text{CO} + s & \rightleftharpoons \text{CO}_s \quad (1) \\
\text{CO}_s + s & \rightleftharpoons \text{C}_s + \text{O}_s \quad (2) \\
\text{O}_s + \text{CO} & \rightleftharpoons \text{CO}_2 + s \quad (3)
\end{align*}
\]

The reversible adsorption of reaction 1 is supported by isotopic substitution studies carried out with $^{12}$CO and $^{13}$CO which indicated an equilibrium between the adsorbed $^{12}$CO with the gas phase $^{13}$CO [93]. Similarly, from this work there is also another equilibrium reaction of:

\[
\text{C}_s + \text{CO}_2 \rightleftharpoons 2\text{CO}_s \quad (4)
\]

The infrared studies showed that this reaction exists under the reaction conditions and it is probably one of the many reactions that maintains the reservoir of CO on the catalyst surface. It is then obvious that the reservoirs of both surface CO and surface carbon (both graphite and carbide) are maintained by the reactions 1 thru 4. Furthermore, the surface oxygen is probably removed by either $\text{H}_2$ or CO. From this work, it is found that CO could act as a reducing agent when the catalyst is rich in oxygen following the reaction 5:

\[
\text{O}_s + \text{CO} \rightarrow \text{CO}_2 \quad (5)
\]
Also when $H_2$ is present, the surface oxygen can be removed by the reaction 6:

$$O_s + H_2 \rightarrow H_2O$$  \hspace{1cm} (6)

One plausible mechanism for the hydrogenation of surface carbon into methane and other long chain hydrocarbons probably proceeds thru the following reaction steps:

$$H_2 + 2s \rightarrow 2H_s$$  \hspace{1cm} (7)

$$C_s + H_s \rightarrow CH_s + s$$  \hspace{1cm} (8)

$$CH_s + H_s \rightarrow CH_2s + s$$  \hspace{1cm} (9)

$$CH_2s + H_s \rightarrow CH_3s + s$$  \hspace{1cm} (10)

$$CH_3s + H_s \rightarrow CH_4 + 2s$$  \hspace{1cm} (11)

$$CH_2s + H_2 \rightarrow CH_4 + s$$  \hspace{1cm} (12)

where $H_2$ must first be adsorbed dissociately on active sites. These atoms of hydrogen later react with nearby carbon to produce psuedo methylene intermediate species, $CH_x$ where $x=1,2,3$. This proposed mechanism follows a similar scheme proposed by Wagner [94] and by Ekerdt and Bell [91]. The mechanism involves the hydrogenation of surface carbon by adding one hydrogen atom at a time. The propagation of 1-carbon species to long chain hydrocarbons can be thought of as a cis migration, where the chain, $Y_n$, forms a bond with insertable species $X$, while the original bond between the adsorbed $Y_n$ and the metal is broken. This idea of stepwise insertion can be represented by the following sequence:

$$CH_3s + CH_2s \rightarrow C_2H_5s + s$$  \hspace{1cm} (13)
\[ C_2H_5s + CH_2s \rightarrow C_3H_7s + s \] (14)

The results have indicated that the product distribution on both Ru and Fe-Ru bimetallic catalysts followed a Schultz-Flory distribution indicating that the propagation of surface hydrocarbon species probably results from a stepwise insertion of "monomer" like species similar to \( CH_x \). Evidence of methylene like vibrational stretching frequencies were observed in infrared studies in this work around 3000 cm\(^{-1}\), and the intensities of these peaks remained constant with time. This led to the conclusion that there might be a methylene like species present during the reaction as an intermediate species.

The reaction sequence as represented by equations 1 through 12 consist of number a of equilibrium reactions between the gas phase and surface species as well as between surface species themselves. Reactions 1 thru 6 have been observed experimentally in this work, both through the infrared studies and thru the kinetic studies. It has been found that these six reaction sequences are fast and occur almost immediately once the catalyst is exposed to the synthesis gas mixture. Similarly, the adsorption of \( H_2 \) was assumed to occur dissociatively and that an equilibrium condition exists between the molecular \( H_2 \) in the gas phase and the atomic \( H \) on the surface. This is supported by the isotopic substitution of \( D_2 \) for \( H_2 \) which showed an inverse isotope effect during the course of the methanation.
reaction. This is a good indication that the dissociation step is fast and not rate limiting. Similar results were also observed by Kellner and Bell [31,95]. Furthermore, the constant intensity of the infrared band for C-H vibrational frequencies with the duration of the reaction led to the belief that the formation of intermediate methylene like species were not the rate limiting steps. Therefore, the rate limiting step must be either reaction step 11 or 12. Using equation 11 as a rate limiting step, Ekerdt and Bell [88] derived the rate expression as:

$$\text{Rate} = k\left(\frac{P_{H_2}^{1.5}}{P_{CO}}\right)$$ (15)

However, if the rate limiting step is reaction 12 then the rate expression would be:

$$\text{Rate} = k\left(\frac{P_{H_2}^{1.5}}{P_{CO}^{0.5}}\right)$$ (16)

which fits our experimental data for catalyst A very well. However, the reaction order with respect to $H_2$ partial pressure deviated from this expression when Fe was added into Ru Y-Zeolite. The order decreased from 1.2 to 0.9 for catalyst B and decreased further to 0.8 for catalyst C. This behavior reflects the lack of numbers of hydrogen active sites in the case of the bimetallic catalysts because the iron oxides have partially covered Ru sites. The hydrogen deficiency of bimetallic catalysts result in a
decrease in the dependency of the rate of reaction on hydrogen partial pressure. This trend was reversed at the heaviest loading of Fe, catalyst D, and the exponential power was restored to 1.1 which is almost to the original value.

In conclusion, it is evident that the mechanism of the methanation reaction is a result of the hydrogenation of surface carbon. The nature of this surface carbon is not clearly defined at this stage, however the surface carbon in the case of pure Ru catalyst probably exists in the form of surface graphite but for Fe-Ru bimetallic catalysts, this carbon reservoir is probably the combination of carbide and graphite. Carbide is most likely associated with the Fe rich particles while the surface graphite is derived from Ru rich particles. This reservoir of carbon is found to be in equilibrium with CO and CO₂ suggesting that the reservoir is being maintained by the disproportionation reaction of adsorbed CO. The nature of adsorbed CO is found to be in the linear form and the surface is always saturated with adsorbate during methanation reaction conditions. The product distribution is found to follow the Schultz-Flory distribution indicating that the formation of long chain hydrocarbons is a result of cis insertion of methylene like species, CH₂. This intermediate species is normally found on the surface of the catalyst under the reaction condition and is evidenced by infrared bands around 3000 cm⁻¹ which remain constant in intensity with the duration of the
reaction. The rate limiting step has been determined to be the hydrogenation reaction of CH$_2$S with H$_2$. This step leads to a rate expression which matches the experimental results. The addition of Fe into the Ru catalyst only affects the nature of H$_2$ adsorption due to the irreducibility of iron oxides. Finally the most striking result of mixing Fe with Ru is a tremendous change in the production rate of CO$_2$. The jump in CO$_2$ production rate is probably the result of a hydrogen deficient surface.
V - CONCLUSIONS

The infrared analysis of CO adsorption on Ru loaded Y-Zeolite at 373 K indicates 3 types of adsorption, namely: bridged adsorption around 1950 cm⁻¹ at very low pressure, linear adsorption at 2046 cm⁻¹ at moderate to high pressure, and multiple adsorption at 2080, 2102, 2137, and 2157 cm⁻¹ at high pressure. However under methanation reaction conditions at 523 K, it was found that the surface of the catalyst is saturated by linearly adsorbed CO which show infrared activity around 2000 cm⁻¹. The multiple adsorption found at 373 K is probably due to the reaction of CO on Ru atoms which occur along the edges and corners of the metal crystallites to produce partially ionized Ru atoms. CO is found to be both an oxidation agent on oxygen deficient surfaces and a reduction agent on oxygen enriched surfaces. The Ru crystallites are found to be very stable when exposed to oxygen at a moderate temperatures. Only surface oxides which can be removed by evacuation at an elevated temperature are formed.

The addition effect of Fe onto Ru is found to reduce the capacity for hydrogen and carbon monoxide uptake by the catalysts. The addition of Fe also produces a decline in the multiple CO adsorption on Ru atoms. This decline is a result of the encroachment of iron oxides onto the Ru particles. The ESCA results and infrared spectra reveal that the iron oxides on the surface of the catalyst
cannot be reduced completely to the metallic state. This difficulty is possibly caused by Ru atoms preventing the migration of iron oxide into a minimum particle size which could be reduced. We also believe that the surface structure of the bimetallic is very different from the bulk of the catalyst. All the available evidence points to surface segregation where Ru and Fe do not enter into a solid solution. They are totally separated from each other and from the isotopic dilution studies these metals are independent of each other. Finally, the addition of Fe to Ru catalysts produces neither a geometrical nor electronic effect on Ru atoms.

The kinetic measurements on the reaction of CO with $H_2$ on Ru and Fe-Ru bimetallic shows changes both in the activity as well as selectivity. Ru loaded Y-Zeolite produces mainly methane and is highly reducible. The Ru metal particles are found to be active toward both hydrogen and carbon monoxide. The high yield of methane can be attributed to the abundance of $H_2$ on the surface of the catalyst. In contrast to the single metal, Fe-Ru bimetals are less reactive to both hydrogen and carbon monoxide. Long chain hydrocarbons are produced more readily on the bimetals. The shift in the selectivity is probably due to a $H_2$ deficiency on the surface of the bimetals, hence allowing chain propagation to occur before chain termination.
The nature of CO adsorption under methanation reaction conditions is found to be the linear form CO-Ru. The surface of the catalyst is saturated with this linearly adsorbed CO. It is found that CO is readily decomposed to C and CO₂ via the disproportionation reaction and an equilibrium exists. It is postulated that there are at least two types of carbon species on the catalyst. Carbon in the graphite form is probably the dominating species in Ru rich particles while the carbide form is probably the common form in Fe rich particles. This surface carbon then reacts with atomic hydrogen which is a result of dissociative adsorption of H₂. An inverse isotope effect was observed when D₂ replaced H₂ indicating that hydrogen disassociative adsorption is not a limiting step. The proposed rate limiting step is then:

\[ \text{CH}_2s + \text{H}_2 \rightarrow \text{CH}_4 + s \]

The rate expression derived from this rate determining step satisfies the experimental data. Chain propagation follows the Schultz-Flory product distribution and is probably a result of cis migration of insertable monomer CHₓ, where x=1,2,3.

A reaction mechanism, consistent with kinetic observations, isotopic experiments, and surface analysis, has been proposed. The reaction sequences are probably initiated by the decomposition of adsorbed CO via the disproportionation reaction. Even though the kinetic results indicate that surface carbon is plausibly the
starting block of this reaction, it is still not clear if this carbon is in the form of graphite or carbide. Since graphite is the most common species for Ru while carbide is the most abundant species in the case of iron, these two distinct forms could possibly influence the product distribution.
VI REFERENCES

2. Fischer, F.; and Tropsch, H.; Brennst.-Chem. 7, 97 (1926).
22. Fischer, F.; Tropsch, H.; and Dilthey, P.; Brennst. Chem. 6, 265 (1925).


ABSTRACT

The catalytic properties of Ru and Fe-Ru bimetallics supported on Y-Zeolite were determined for the CO hydrogenation reaction. The results, based on the reaction at 523 K and an \( \text{H}_2 : \text{CO} \) ratio of 3:1, revealed that the addition of Fe to Ru effectively reduces the number of both \( \text{H}_2 \) and CO active sites as determined by chemisorption experiments. Based on \( \text{H}_2 \) chemisorption, the dispersion (number of active sites per total number of metal atoms) decreased from 0.59 with no Fe present to 0.02 with 5.9% Fe. This phenomenon was substantiated by the ESCA analysis which indicated totally reduced Ru metal particles in both Ru and Fe-Ru bimetals, however iron oxides could not be reduced to their metallic state.

The addition of Fe also influences the product distribution. An increase in Fe content reduces the amount of methane while increasing the amount of long chain hydrocarbons. Furthermore the product distribution follows the Schultz-Flory distribution. This observation is probably due to surface \( \text{H}_2 \) deficiency encouraging chain propagation instead of chain termination. The rate determining step is the hydrogenation of surface methylene...
species.

The infrared analysis of CO adsorption on Ru catalyst at 373 K indicates 3 types of adsorption: bridge adsorption at 1950 cm$^{-1}$, linear adsorption at 2046 cm$^{-1}$, and multiple adsorption at 2089, 2102, 2137, and 2157 cm$^{-1}$. However under methanation reaction conditions at 523 K, it was found that the surface of the catalyst was saturated by linearly adsorbed CO around 2000 cm$^{-1}$. The infrared experiments as well as the isotopic dilution experiment point to surface segregation where Ru and Fe do not enter into a solid solution. Finally, the addition of Fe to Ru catalysts produces neither a geometrical nor an electrical effect on Ru atoms.
VITA

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