3.5 Surface Structure Sensitivity

3.5.1 Reaction Sensitivity

It is important to mention the role that surface structure sensitivity plays in the analysis and interpretation of the data gathered in this work. In general, CO hydrogenation is considered to be structure insensitive [13, 56]; that is, the reaction rate is independent of the arrangement of surface atoms, metal particle size and support used. For this reason, it is assumed that each surface atom in this study represents an active surface site, or at least that the total number of surface atoms and active sites are directly proportional [56].

The structure insensitivity of nickel surfaces for CO hydrogenation is well documented [15, 24, 30, 57-61, 62] for a variety of both supported catalysts and single crystals. There has been less agreement among researchers studying other Group VIII metals, with evidence for crystallite size, metal loading (and thus dispersion) and support effects [13, 63-64]. More recently, however, several studies on Fe, Co, Ni, Mo, Ru and Rh [62-69] have shown that pure, well-reduced catalysts can yield rates which are independent of dispersion and surface structure. For example, Kelley and Goodman [62] found very similar rates and activation energies for methanation over the Ru(110) single crystal and the Ru(001) basal plane, which have quite dissimilar structures.

Therefore, if it assumed that findings which suggest CO hydrogenation to be structure insensitive are extended to include ruthenium catalysts such as those in this study, the only further consideration required to allow for comparison of specific rates is accurate determination of the metal dispersion of these catalysts. For this reason, dispersion values were obtained from an optimized H_2 chemisorption technique, as described in the Section 4.

3.5.2 Adsorption Sensitivity

Although the term structure sensitivity is usually used in reference to the sensitivity of surface reactions to surface structure, adsorption processes have also been shown to be structure sensitive. Since adsorption and dissociation on a surface atom are strongly dependent on the electronic environment of the atom, and this environment is strongly affected by neighboring atoms, it is not surprising that sites with different coordination exhibit different adsorption characteristics. For example, Bernasek [70] has reported that hydrogen adsorption and dissociation occur more efficiently at low coordination sites on platinum.

3.6 Bimetallic Ruthenium Catalysts

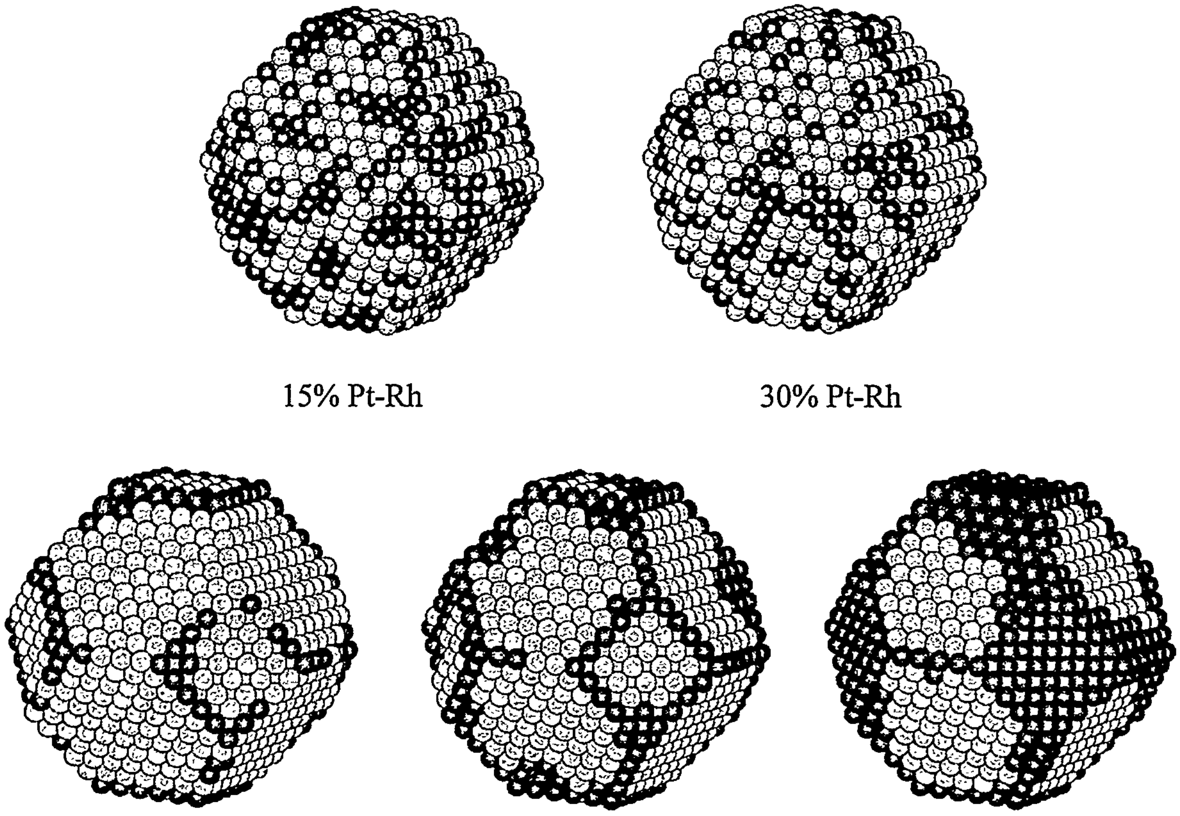
The utility of ruthenium as a constituent in FTS catalysts is evident in the unique characteristics of bimetallic catalysts containing ruthenium and another metal. Several patents have been granted for Co-Ru [71-73] and Re-Ru [74] commercial catalysts, and there have been many studies on Os-Ru and Fe-Ru systems (see discussion in [13]). Mori [75] reported increased CO dissociation rates during FTS upon addition of V or Mo to alumina supported Ru. Enomoto [76] noted suppression of CH_4 formation with V added to Ru/Al_2O_3. More recently, researchers in Russia have examined an alumina-supported Co-Ru catalyst for

CO hydrogenation [18], and Kintaichi and coworkers [77] examined silica-supported Ir-Ru catalysts to produce C_2 oxygenates via CO hydrogenation.

An important and interesting phenomenon in heterogeneous catalysis is the synergistic effect often observed upon addition of Group IB metals (Cu, Ag and Au) to transition metal catalysts. While the added metal may not interact directly with the adsorbed species during reaction, their effect on reaction catalytic behavior is often more than the sum of the individual contributions of the two metals. Thus, the Group IB metal apparently affects the activity of the transition metal without necessarily directly taking place in the reaction itself.

A considerable amount of research has been conducted on Cu-Ru catalysts [45, 50, 78-98], but less is known about Ag-Ru [46, 51, 76, 88, 96, 99-100] and Au-Ru [44, 101] catalysts. In general, the addition of Cu to Ru catalysts for CO hydrogenation dramatically decreases the activity [78, 84, 88-90], changes the product selectivity [78, 89, 90], and sometimes shows an increase in activation energy [88, 89]. In most of these studies, ensemble effects were ruled out as a source of the synergistic activity.

The Ag-Ru bimetallic system is of particular interest in CO hydrogenation studies due to the fact that that silver does not appreciably adsorb either hydrogen or carbon monoxide [102] and thus does not take part in surface reactions.. In addition, hydrogen adsorbed on ruthenium does not spill over to silver. It is also advantageous to utilize the fact that Ag atoms preferentially occupy certain locations in bimetallic ruthenium particles. Monte-Carlo simulations of Group IB-Ru systems conducted by our group [88, 100] reveal that Cu, Ag and Au atoms migrate to the surface of bimetallic particles, tend to cluster with like atoms, and preferentially occupy low-coordination edge, corner and other "defect-like" sites. Figure 1 [100] shows the results of several simulations which demonstrate this behavior. In contrast to systems like Pt-Rh (top row), which exhibit random mixing of platinum atoms (light spheres) with rhodium atoms (dark spheres) at all loadings, bimetallic systems such as Cu-Ru(bottom row) exhibit strong segregation of copper atoms (dark spheres) from ruthenium



15% Pt-Rh

30% Pt-Rh

5% Cu-Ru

10% Cu-Ru

15% Cu-Ru

Figure 1. Monte-Carlo atomistic simulation of bimetallic particles (Strohl and King 1989)

atoms (light spheres). The Group IB atoms segregate in three ways: they tend to migrate out of the bulk to locations on the catalyst surface, they tend to group together with other IB atoms, and they preferentially occupy low-coordination edge and corner sites. In Ag-Ru bimetallic systems, nearly complete occupation of these sites occurs at Ag contents below 20 atomic % (total metal) [88]. Ensemble effects in Ag-Ru catalysts are also not believed to be operative, as Ag does not break up ensembles in Ru [96, 100, 103]. Electronic effects, which may affect the vacant *d* orbitals in Ru, are also not believed to be present [48, 99]. Therefore, other mechanisms which explain the behavior of Ag-Ru catalysts must be investigated.

4. TECHNIQUES

4.1 Preadsorbed CO Reaction Techniques

For this study, carbon monoxide is preadsorbed onto the catalyst surface prior to reaction. In this way, a surface initially saturated with CO is achieved, and upon exposure to hydrogen gas at reaction temperatures, the initial rate of methane formation is a measure of the surface activity. This method has several important advantages over steady-state or coadsorption techniques:

1. since CO and H_2 are not simultaneously adsorbing, the effects from CO/H_2 coadsorption mentioned earlier are not present;
2. the influence of CO adsorption is removed from the kinetic analysis;
3. since the surface is not resupplied with CO, the product distribution consists solely of methane, and the rate analysis is simplified;
4. the partial pressures of products are small, and thus their desorption does not enter into the kinetic analysis;
5. deactivating effects common in steady-state reaction techniques are not present under these conditions; and
6. a secondary result of the experiment is that the surface carbon is quantitatively analyzed by way of hydrogen titration as long as the reaction is driven to completion.

The generalized chemical equation for this process may be represented as:

$$M\text{-}CO + H_2 \rightarrow CH_4 + H_2O$$

The rate measured this way is done so without exact knowledge of which step in the reaction mechanism it represents. This is important to the analysis of data when it is possible that the rate-limiting process may be changing upon addition of Ag to the Ru catalyst, as will be discussed later.

This technique has been successfully applied by several other researchers. Dwyer [33] and Sexton [34] conducted hydrogenation studies over Rh, Fe and Ni by predepositing CO via the Boudouard reaction, evacuation and subsequent hydrogenation. Rabo [31] and Wentreck [32] utilized hydrogen titration to calculate the amount of surface carbon present on Co, Ni, Ru and Pd from the amount of CH_4 formed during hydrogenation. Biloen [30] utilized an isotopic method to dissociatively adsorb ^{13}CO, followed by reaction with CO/H_2 mixtures. Biloen and Sachtler [3] reviewed hydrogenation of preadsorbed CO in detail, and Goodwin *et. al.* [25] recently studied methanation over Ru/SiO_2, noting that such studies are directly relevant to hydrogenation reactions because the rate-limiting steps, usually hydrogenation of surface carbon species, are the same. Also, similar temperature-programmed surface reaction (TPSR) methanation studies where preadsorbed CO is reacted with hydrogen have been conducted by many researchers, and the results have been found to correlate well with steady-state experiments (see, for example, [104]).

Finally, the following guidelines [56] recommended for reproducible rate measurements were used:

1. under the experimental conditions used in this study, the CO conversion was low during the steady-state portion of the experiment (typically less than 5%);

2. mass and heat transfer limitations were found to be present only at higher temperatures, and when these limitations were evident, the data was not used in further kinetic analysis;
3. catalyst deactivation was monitored by tracking total methane formation through a calibration factor for each experiment with a given catalyst sample;
4. specific rates are reported as turnover frequencies, TOF (also known as turnover rate, TOR) in units of moles CH_4 formed per mole active site (surface Ru atom) per second; and
5. the widest possible temperature range was utilized.

4.2 Catalyst Preparation

Silica-supported ruthenium catalysts containing 4% (by weight) ruthenium metal were prepared from solutions of 1.5% ruthenium nitrosyl nitrate (Strem Chemicals). The incipient wetness preparation technique was used by impregnating Cab-O-Sil silica (BET surface area 300 m^2/g) with the ruthenium solution to form a slurry, which was allowed to dry at room temperature overnight and then at 383 K for two hours. The Ru-Ag bimetallic catalysts, containing 3, 10, 20 and 30% (atomic percent of total metal) silver metal, were prepared by coimpregnation of $AgNO_3$ with the ruthenium solution. The ruthenium loading in the bimetallics remained at 4 wt.%. The catalyst samples were then washed with hot deionized water to remove sodium and chlorine contamination. In most cases, the same catalyst samples that were used in previous microcalorimetry studies were used in this study. For the ^{1}H-NMR experiments, a catalyst sample prepared for an earlier study [105] was used.

4.3 Dispersion Measurements

All catalyst dispersions were measured by hydrogen chemisorption using a custom-built adsorption apparatus described previously [49]. An optimized volumetric technique from Uner [48] was used for the chemisorption experiments. After reduction, the catalyst sample was cooled to 335 K and exposed to successive doses of hydrogen for 10 minutes at pressures from 10 to 100 torr. Two isotherms, for total and weakly bound hydrogen, are obtained. The weakly bound hydrogen isotherm is obtained by evacuating the sample for 10 minutes between doses. By extrapolating the linear portions of these isotherms to 0 torr, the amount of strongly bound hydrogen present could be calculated from the difference in intercepts. The catalyst dispersion is then calculated from this quantity.

For the ^{1}H-NMR experiments, a catalyst sample used in earlier studies [105] was used. The dispersion for this catalyst was determined via ^{1}H-NMR, which has been shown to correlate well with dispersions obtained from the optimized volumetric technique [48]. Dispersion values for the catalyst samples used in this study are presented in Table 1.

TABLE 1. Catalyst sample dispersions

catalyst[a]	**volumetric dispersion**
4% Ru/SiO_2	0.261
4% Ru/SiO_2 (NMR)	0.20[b]
3% Ag-Ru/SiO_2	0.258
10% Ag-Ru/SiO_2	0.121
20% Ag-Ru/SiO_2	0.180

[a] all catalysts contain 4 weight percent ruthenium; silver content shown are atomic percent of total metal

[b] determined via ^{1}H-NMR

4.4 ^{1}H-NMR Experimentation

The nuclear magnetic resonance (NMR) experiments utilized a custom-built spectrometer operating at a proton resonance frequency of 250 MHz and utilizing a spin-temperature inversion pulse technique. This apparatus is the same as that described elsewhere [43], except for the addition of a digital PC interface to control pulse programming and data signal conversion and acquisition through a Nicloet 430 digitizer. A scan rate of 0.1 seconds/scan was utilized with 100 scans/average. Between 2 and 10 averages were gathered for each spectra, for a total of 200 to 1000 scans per spectra. A custom Pyrex *in situ* probe containing a catalyst sample was used for dynamic measurements of hydrogen surface coverages on the catalyst surface during reaction with preadsorbed carbon monoxide.

4.5 Catalyst Pretreatment

About 0.25-g of each catalyst was weighed, loaded into a Pyrex reaction cell, and reduced *in situ* by successively exposing the catalyst to one atmosphere of hydrogen in successive 30 minute doses for a total of 2 to 3 hours at 673 K. The sample was evacuated for 2 to 3 hours at 673 K, and then overnight at room temperature. This procedure was conducted between each experimental reaction run.

Prior to reaction, the catalyst was exposed to 1 atmosphere of CO at room temperature for 1 hour. The cell was then evacuated for 30 minutes to remove weakly-bound CO, followed by heating to reaction temperatures.

4.6 Experimental Apparatus

A custom glass and stainless steel reaction and adsorption manifold, shown in Figure 2, was constructed to conduct the kinetic studies. The manifold was supplied through a multiport stream selection valve with research-grade hydrogen (Spectra Gases, 99.9995%)and carbon monoxide (Matheson, 99.99%) and zero-grade helium (Air Products, 99.999%), which were further purified with Drierite and molecular sieve gas purifiers (Alltech), activated carbon hydrocarbon traps and oxygen traps (Alltech). In addition, the hydrogen stream was passed through a liquid nitrogen trap. The manifold was wrapping in heating tape and maintained at an elevated temperature to minimize gas adsorption on the inner surfaces. A Balzers TPH-60 turbomolecular pump, backed by a Welch Duoseal mechanical pump, was used for evacuation. Pressures in the manifold were measured with Baratron pressure transducers (MKS Instruments). A custom Pyrex reaction cell, connected to the manifold via Ultratorr (Cajon) vacuum fittings, was placed inside a custom-built furnace connected to an Omega 6100 temperature controller. A type K chrome-alumel thermocouple in the furnace provided temperature feedback to the controller for isothermal operation.

The sample cell was connected to a custom high-vacuum stainless steel manifold via a needle valve and 0.32-mm×1-m nonpolar fused-silica capillary (Supelco), both of which were maintained at an elevated temperature. The manifold contained a UTI 100C quadrupole mass spectrometer probe utilizing an open source ionizer and electron multiplier. It was determined that a filament emission current of 0.58 milliamps minimized species fragmentation while providing sufficient ionization sensitivity. Using an Omega CN-800

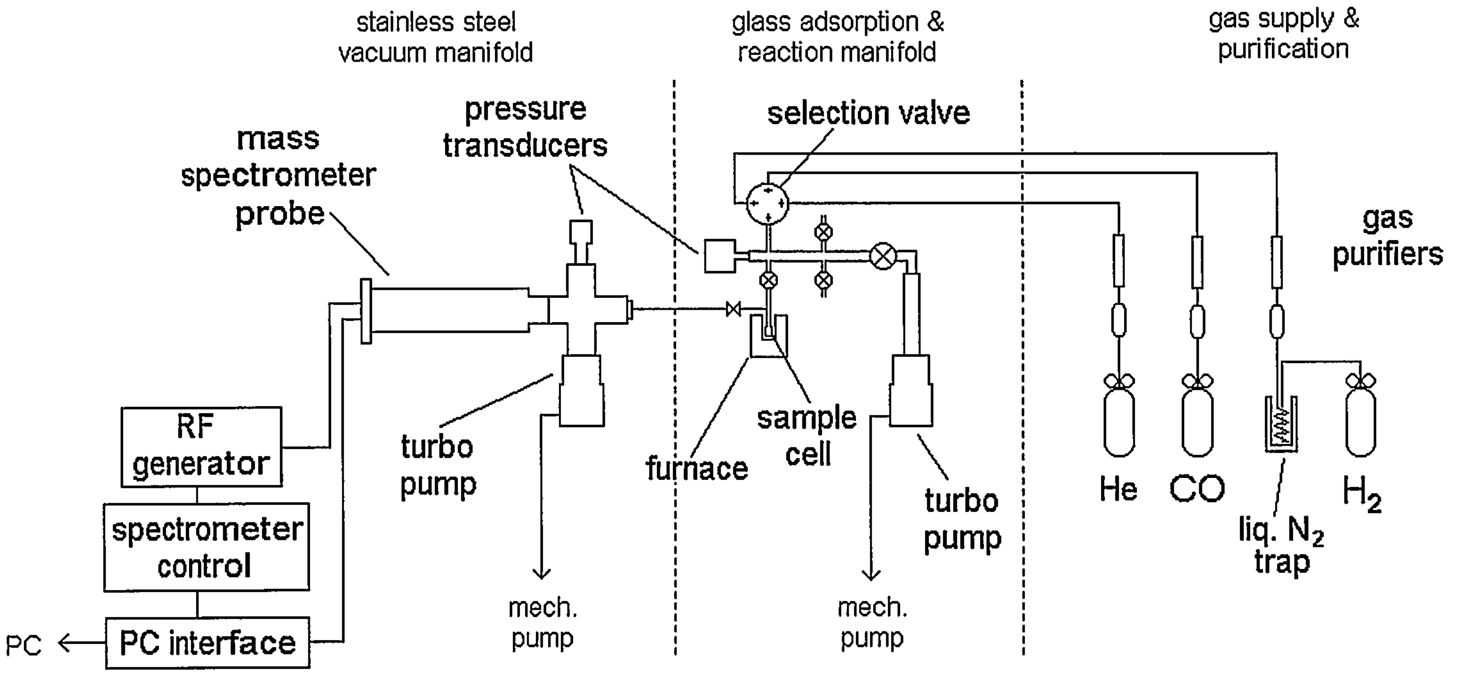


FIGURE 2. Experimental apparatus

temperature controller and type J thermocouples, the manifold was maintained at about 425 K during experimentation to avoid condensation of sample species, and could be baked-out between experiments at 575 K. A Balzers THS-065 pumping station allowed evacuation of the manifold to about 2×10^{-6} torr, as measured by a Varian 531 thermocouple gauge and a Varian 525 cold cathode gauge. A UTI SpectraLink interface was used to connect the spectrometer to an Hewlett Packard Vectra computer for control and data acquisition using Hewlett Packard SpectraSoft software.

4.7 Experimental Reaction Methods

After reduction of the catalyst surface and CO adsorption, catalyst samples were evacuated at room temperature for 30 minutes. The sample cell was then heated to reaction temperature, between 400 K and 525 K, and exposed to 460 torr of hydrogen while monitoring the reaction with the spectrometer. Under these conditions, with essentially no gas-phase CO present, the only carbon reaction product is CH_4. Hence, masses 2 (H_2), 15 (CH_3), 18 (H_2O), 28 (CO) and 44 (CO_2) were monitored. The fragment mass 15 was used to monitor CH_4 instead of 16 in order to avoid interference from O fragments from H_2O and CO. Experiments using a pure methane standard showed that this fragment formed in the ionizer of the spectrometer in levels directly proportional to the parent mass 16, so that it could be used for calibrations. While maintaining the hydrogen pressure at 460 torr, data was gathered for about 20 minutes, until the initial linear responses from CH_4 and H_2O leveled. The sample was then heated to 673 K to drive the surface reaction to completion so that the total amount of carbon species initially present on the catalyst could be calibrated to the spectrometer signals. After reaction, the sample was then reduced in hydrogen, according to the procedure outlined above, prior to the next experiment.

The order of metal loadings for the Ag-Ru bimetallics, as well as the temperatures used for each run, was randomized to eliminate any effects of catalyst deactivation or hysteresis in the data. In addition, each metal loading and temperature combination was reproduced at least once. A detailed listing of the order used in randomizing these experimental values is given in the Appendix.

4.8 Data Analysis

All spectrometer signals were first corrected for baseline drift occurring during the course of each experiment, and then normalized with respect to the H_2 signal. Despite the rapid initial signal response, the latter was necessary due to the long time required for a steady-state signal to be achieved upon admission of H_2 to the reaction chamber. It was assumed that all the species monitored would require similar time to achieve a steady-state signal, and the normalization removed this characteristic from the experimental data.

Calibration of the methane signal from the spectrometer is done by calculating the total area under the methane signal and from knowledge of the C:M ratio of the adsorbed CO (Section 3.2) and the catalyst dispersion. This information, coupled with the linear portion of the methane response allowed calculation of initial turnover frequencies (TOF) in moles of methane formed per mole of surface ruthenium atom per second. The linear portion of each set of data was identified and the slope determined by linear regression. The data points to be included in the regression set were selected based on minimization of the standard deviation of the regression slope. This slope is directly proportional to the rate for the process under examination and is expressed without knowledge of the specific surface processes it represents.

In some cases, anomalous data points were rejected from further kinetic analysis based on one or more of the following criteria:

1. the measured rate constant at a given temperature was found to yield a TOF which deviated significantly from an established linear trend over the temperature range studied for each sample;
2. the calibration factor, determined from the total area integration, deviated significantly from a constant value which was unique to each catalyst sample; and/or
3. the data point was not reproducible in later experimentation.

The first condition was found to occur in cases when either too few data points were gathered during the steady-state portion of the experiment or when sufficiently isothermal operation was not achieved. The second condition was common when an improper emission current was used during experimentation or when reduction was incomplete. When these criteria required elimination of a suspect data point, the experiment was reconducted until a reproducible result was determined.

The apparent activation energy for the process under investigation is then calculated for each catalyst using an Arrhenius relation and plotting the natural log of the TOF versus the inverse absolute temperature and performing a linear regression of the data.

The ^{1}H-NMR spectra peaks corresponding to adsorbed hydrogen and silica support hydroxyl groups were deconvoluted by computer assuming symmetry around the hydroxyl peaks. After deconvolution of these peaks, the areas under the hydrogen-on-ruthenium peaks where calculated to correlate with the hydrogen uptake by the catalyst. Relative intensities for the two types of peaks were calculated by assuming that the hydroxyl group peak height remained relatively constant on the time scale of the experiments. This approximation has been confirmed in earlier studies by our group.