1. RESEARCH OBJECTIVES

Although the catalytic hydrogenation of carbon monoxide has been a subject of considerable investigation for many years, its increasing economical attractiveness as an industrial source of hydrocarbons has recently led to a search for more active and selective catalysts. A fundamental problem in the development of such catalysts is an incomplete knowledge of the operative surface processes, due in large part to the inability to accurately measure surface concentrations of reactant species during reaction. Specifically, the concentration of surface hydrogen proves difficult to estimate using normally revealing techniques such as transient isotopic exchange due to kinetic isotope effects. Knowledge of such concentrations is essential to the determination of the mechanisms of adsorption and reaction, since many kinetic parameters are concentration dependent.

It is the aim of this research to investigate the mechanism and kinetics of the adsorption and reaction of hydrogen on silica-supported ruthenium and silver-ruthenium catalysts during the hydrogenation of carbon monoxide. The specific activity of ruthenium in Group IB-ruthenium bimetallic catalysts is known to decrease dramatically upon addition of the Group IB metal, even though these metals do not directly adsorb or react with hydrogen or carbon monoxide. Since silver is known to selectively occupy low-coordination sites in silver-ruthenium bimetallic systems, it can be used as a tool to block these sites from adsorption and reaction. In this way, any differences between the kinetics of processes occurring at these sites can be resolved. The mechanism of this synergistic effect will be elucidated in terms of a "portal site mediated adsorption" model. Previous work by our group has proposed that hydrogen adsorption occurs via a mechanism where low-coordination "portal" sites on the catalyst serve as locations for rapid, dissociative adsorption of hydrogen to supply the surface with hydrogen for reaction with carbon monoxide.

By preadsorbing carbon monoxide onto the surface of ruthenium and silver-ruthenium catalysts, the kinetics of hydrogen adsorption and reaction can be monitored upon exposure of this surface to ambient hydrogen gas. This is accomplished by conducting identical experiments on two separate systems. First, the formation of methane is monitored using mass spectroscopy, and specific reaction rates and apparent activation energies are measured. Next, *in situ* ^{1}H-NMR is used to monitor the amount of hydrogen present on the catalyst surface during adsorption and reaction. The results for these two sets of experiments are then combined to show a correlation between the rate of reaction and the surface hydrogen concentration. Finally, transition state theory is applied to this system and is used to explain the observed change in the apparent activation energy. The structure sensitivity of hydrogen adsorption on ruthenium is then elucidated by comparison of these results with differential heats of hydrogen adsorption data for the two systems.

The importance of this work cannot be overemphasized. For the first reported time, measurement of surface hydrogen concentrations during reaction has given new insight into the kinetics and mechanisms of adsorption and reaction of hydrogen on supported metal catalysts. The results of this study support a new model for hydrogen adsorption on these catalysts which may prove applicable to other systems. Since hydrogen is one of the most widely used reactant species in industrial catalytic processes, the implications of this work are far reaching and of great significance to applied research in this area.

2. INTRODUCTION

Since Sabatier and Senderens [1] first produced methane by reacting hydrogen and carbon monoxide over a nickel catalyst in 1902, the catalytic hydrogenation of carbon monoxide over the Group VIII transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) has been an area of increasing focused research for nearly a century. Fischer and Tropsch [2] reported on the synthesis of higher hydrocarbons using iron and cobalt catalysts in 1923, and today the term Fischer-Tropsch synthesis is reserved for processes which produce C_2 and higher hydrocarbons (usually linear alkanes and alkenes) and/or oxygenates (usually *n*-alcohols), as opposed to methanation processes, where methane is the primary product. While the two processes often occur separately in industry and are sometimes treated separately in literature, they are intimately linked due to the fact that both processes depend strongly on interactions between similar catalyst surfaces, reactants and adsorbed intermediates.

Fischer-Tropsch synthesis (FTS) is the only existing major alternative to petroleum and natural gas as a source for liquid hydrocarbon petrochemicals. Because the volumetric energy content of such liquids is significantly greater than gaseous hydrocarbons, and because their combustion produces less pollution than solid fuels, their importance in industry cannot be overstated [3]. At present, industrial FTS processes are the third largest consumer of syngas [4]. As coal gasification technologies and steam reforming process for natural gas become more advanced, the use of syngas as a source of carbon monoxide and hydrogen for FTS is becoming increasingly economically feasible. Currently, it is estimated that coal and natural gas reserves outweigh those of crude oil by 9:1 [5]. The waxes produced from FTS are used in many industries, do not contain aromatic, nitrogen or sulfur impurities, and are well regarded for their high quality and stability [6].

BASF first patented high-pressure CO hydrogenation in 1913 and constructed the first industrial FTS plant in 1935 in Germany [4]. In the United States, Hydrocarbon Research briefly operated a FTS plant in Texas in 1950 [5]. Beginning in 1955, the South African Sasol plants were the only major producers of hydrocarbons via FTS for many years, with a total capacity of about 4 million tons annually [7], until more recently, when several new FTS facilities have come on-line. These include a Mobil MTG unit in New Zealand (1985) which produces methanol and high-octane gasoline, a South African Mossgas (1992) gasoline and diesel fuel production facility, Shell's Malaysian MDS (middle distillate synthesis) plant (1993) for high-quality diesel fuels and waxes, and a new Mossgas plant in South Africa (1996) [5, 8]. In addition, Sasol recently patented a new slurry bubble-column reactor (1994), and both Sasol and Exxon are currently conducting feasibility studies in Qatar to process offshore gas reserves [9]. The market is even expanding enough to allow smaller companies to enter, such as the Oklahoma based Syntroleum, that has developed and licensed a new FTS process to Marathon and Texaco (1997), and Rentech, a Colorado company that is currently licensing its process to Texaco and constructing a FTS facility in India.

The approach of companies who are developing Fischer-Tropsch process is two-fold, simultaneously examining new process designs while incorporating novel catalyst to target specific products. While the exact composition of the catalysts used in these industrial facilities are proprietary, all contain iron, cobalt or a combination of the two metals, often with promoters to increase the selectivity of a particular product. Clearly, the resurgence of Fischer-Tropsch synthesis in industry is an indicator of the increasing viability of this process as more advanced catalysts and techniques make production of hydrocarbons via this route more economically attractive.

3. HYDROGENATION OF CARBON MONOXIDE

Several authors have written excellent reviews in recent years of the catalytic hydrogenation of CO. Among these are the summaries of kinetic information by Vannice [10] in 1976 and Wojciechowski [11] in 1988, and the mechanistic review of Biloen and Sachtler [3] in 1981, which includes a lengthy discussion on the hydrogenation of deposited surface carbon, a technique employed in this study. More recently, *Topics in Catalysis* dedicated an entire issue [12] to industrial hydrocarbon production, and Adesina [8] reviewed catalyst design, reaction kinetics and mechanisms, and industrial reactor development. In addition, there have been recent general reviews on the Fischer-Tropsch synthesis by Dry [5] and Bartholomew [13] and on reactions of syngas by Wender [4]. More relevant to the present study, Somorjai [14] reviewed the catalytic synthesis of methane and methanol via CO hydrogenation.

In general, the Group VIII transition metals and their oxides are good hydrogenation catalysts, and the modern work of Vannice [15] shows that the metals used by early researchers as catalysts were good choices. Vannice measured the activity of the Group VIII transition metals (except osmium) towards CO hydrogenation to methane as decreasing in the order:

$$\mathrm{Ru} > \mathrm{Fe} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Rh} > \mathrm{Pd} > \mathrm{Pt} > \mathrm{Ir}$$

This trend is reflected in these catalysts' selectivity toward higher hydrocarbons, with the average carbon number decreasing similarly:

$$\mathrm{Ru} > \mathrm{Fe} > \mathrm{Co} > \mathrm{Rh} > \mathrm{Ni} > \mathrm{Ir} > \mathrm{Pt} > \mathrm{Pd}$$

The major drawback for ruthenium as a commercial FTS catalyst is its cost compared to Fe or Co, although there have been promising tests of its use in FTS and ammonia synthesis reactors. Accordingly, commercial processes utilize iron and cobalt catalysts for FTS, with nickel serving as a methanation catalyst. In addition to their low cost and ability to produce high carbon number products, iron and cobalt catalysts do not form large amounts of oxygenated hydrocarbons, and they have low activities towards the water-gas shift reaction. Cobalt has the advantages of requiring lower reactor pressures and, unlike iron, deactivating elemental carbon does not deposit on the surface during reaction. In addition, the selectivity of cobalt toward straight-chain hydrocarbons is higher.

Nevertheless, the importance of ruthenium as a model surface for studying its exceptional properties has made it the subject of substantial investigation, especially in recent years [6, 16-18]. As the most active Group VIII transition metal, ruthenium is active at temperatures as low as 373K, produces the largest hydrocarbons, does not form oxide phases with catalyst supports [19] and provides researchers with simple product distributions. In addition, under most conditions, inactive carbide formation does not occur on the metal surface. Perhaps most importantly, carbon monoxide dissociates easily and at lower temperatures than other active Group VIII metals, resulting in very low oxygenate formation compared to Os, Rh, Ir, Pd and Pt, on which carbon monoxide does not usually dissociatively adsorb [14, 20].

3.1 Mechanism and Kinetics

3.1.1 Fischer-Tropsch Synthesis

The mechanism of carbon monoxide hydrogenation consists of five primary steps: reactant adsorption, chain initiation, chain growth, chain termination and product desorption. Most frequently, these steps are commonly proposed to occur via five types of mechanisms, which differ primarily in the nature of the proposed intermediate species present on the catalysts during reaction: surface carbide, enolic intermediate, CO-insertion, alkoxy intermediate, and combination mechanisms. In recent years, combination mechanisms which utilize a carbidic intermediate surface species coupled with CO-insertion seem to be gaining the most support. Mechanisms proposed by Dry [5, 7, 21] and Somorjai [14] meet these requirements, and are examples of "flexible" mechanisms that can explain the behavior of a variety of catalyst surfaces. Dry's mechanism [5] is given below:

- adsorption and dissociation

$$CO \leftrightarrow M\text{-}CO \rightarrow M\text{-}C + M\text{-}O$$
$$H_2 \leftrightarrow 2\ M\text{-}H$$

- initiation

$$M\text{-}C + M\text{-}H \rightarrow M\text{-}CH + M\text{-}H \rightarrow M\text{-}CH_2$$

- propagation

$$2\ M\text{-}CH_2 \rightarrow M\text{-}CH\text{-}CH_3 \rightarrow \rightarrow M\text{-}CH\text{-}CH_2\text{-}R$$

and/or

$$2\ M\text{-}CH_2 \rightarrow \rightarrow M\text{-}CH\text{-}R + M\text{-}CO \rightarrow M\text{-}C(CH\text{-}R)\text{-}O\text{-}M + 2\ H_2 \rightarrow M\text{-}CH\text{-}CH_2\text{-}R + H_2O$$

- termination

$$M\text{-}CH\text{-}CH_2\text{-}R \rightarrow CH_2{=}CH\text{-}R$$

$$M\text{-}CH\text{-}CH_2\text{-}R + 2\ M\text{-}H \rightarrow CH_3CH_2\text{-}R$$

$$M\text{-}CH\text{-}CH_2\text{-}R + M\text{-}O \rightarrow R\text{-}CH_2CHO\text{-}M + M\text{-}OH \rightarrow R\text{-}CH_2COOH$$

$$M\text{-}CH\text{-}CH_2\text{-}R + 2\ M\text{-}H + M\text{-}CO_2 \rightarrow R\text{-}CH_2CH_2COOH$$

and/or

$$M\text{-}C(CH\text{-}R)\text{-}O\text{-}M + 2\ M\text{-}H \rightarrow R\text{-}CH_2CHO$$

$$M\text{-}C(CH\text{-}R)\text{-}O\text{-}M + 2\ H_2 \rightarrow R{=}CH_2$$

$$M\text{-}C(CH\text{-}R)\text{-}O\text{-}M + M\text{-}OH + M\text{-}O \rightarrow R\text{-}CH_2COOH$$

Methane can form at any time during the course of chain propagation if hydrogen is present in sufficient surface concentrations to completely hydrogenate a surface carbon species:

$$M\text{-}CH_2 + M\text{-}H \rightarrow M\text{-}CH_3 + M\text{-}H \rightarrow CH_4$$

While methane is the thermodynamically favored product under all conditions, the ability to suppress this reaction in favor of chain growth is the hallmark of a good Fischer-Tropsch catalyst. In the absence of gas phase CO, as in CO preadsorption techniques, methane is formed almost exclusively [3].

Depending on the catalyst used, not all steps necessarily take place on the surface [8], as the energetics of surface adsorption and dissociation vary not only from one metal to another, but from one surface face to another. In addition, the reactions shown are not necessarily the only ones that can occur on the catalyst surface. For example, a side reaction has been seen on nickel at 600 K, when Rabo [22] reacted activated carbon with water:

$$2\ M\text{-}C^{*} + 2\ H_2O \rightarrow CO_2 + CH_4$$

Other common side reactions include the water-gas shift reaction,

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

(a beneficial reaction in hydrogen-poor feedstock), the Boudouard disproportionation,

$$2\,CO \rightarrow C + CO_2$$

and high-temperature, deactivating coke deposition

$$H_2 + CO \rightarrow C + H_2O$$

The extent to which these side reactions occur can be controlled to some extent by catalyst selection, the use of promoters, and operating conditions. For ruthenium catalysts, the water-gas shift reaction does not usually occur to a significant extent, and coke deposition is much less than for any other metal, probably due to the ease of CO dissociation on Ru.

An interesting result of kinetic analysis of the FTS mechanism is that often the same governing equation results from different mechanistic derivations. Two forms of rate equations are generally agreed to accurately describe the kinetics on FTS and methanation catalysts. A power rate law for the rate of CO consumption, r_{CO}, can be expressed as follows:

$$r_{CO} = k\,P_{H_2}^{\alpha}\,P_{CO}^{\beta} \tag{1}$$

where k is the rate constant, P is the partial pressure of H_2 or CO, and α and β are the reaction orders of H_2 and CO, respectively. The Langmuir-Hinshelwood (LH) relation supports the generally accepted opinion that the rate-determining step is bimolecular [8]:

$$r_{CO} = \frac{k\,P_{H_2}^{a}\,P_{CO}^{b}}{\left(1 + \sum_{i=1}^{n} K_i P_{H_2}^{c_i}\,P_{CO}^{d_i}\right)^2} \tag{2}$$

where a and b are the H_2 and CO molecularities of the rate determining step, c_i and d_i are their surface coverage constants for the ith term in a mechanism consisting of n steps, and K_i is the equilibrium adsorption constant for that step. General observations for the parameters in these expressions show that the rate is generally positively related to H_2 partial pressure and that the CO dependence varies from -1 to 0.5, depending on the H_2:CO ratio. In fact, several models fit kinetic observations, and the fact that the variation in hydrogen reaction order in the LH expression is independent of the rate-determining step can be attributed to the weakness of hydrogen adsorption compared to that of carbon monoxide [3].

However, these equations reflect an underlying problem in the development of kinetic expressions, where macroscopic parameters such as partial pressures are used to describe processes which involve microscopic processes such as adsorption, dissociation and surface diffusion. This is primarily due to that fact that many microscopic parameters, such as surface species coverages on the catalyst, are difficult to measure during reaction. Therefore, researchers are forced to either estimate such parameters, or relate the rate to macroscopic parameters. Such is the case for steady-state isotopic transient kinetic analysis (SSITKA) studies, where kinetic isotope effects do not allow accurate calculation of hydrogen coverages during reaction.

3.1.2 Methanation

For the present discussion, an approach similar to that of Alstrup [23] for methanation over nickel is used to develop a "microkinetic" model of the hydrogenation of carbon monoxide to methane. First, the following assumptions are made:

1. under experimental conditions of low conversion, reactions involving CO_2 are not important;
2. knowledge of sticking probabilities for H_2 and CO reveal that their rates of adsorption are usually rapid compared to methane formation [24];
3. the formation and desorption of H_2O from adsorbed oxygen is also rapid, and so CO dissociation is assumed to be irreversible;
4. under conditions of low conversion and small methane partial pressures, the formation and desorption of methane is also assumed to be rapid and irreversible.

Note that the second assumption, for rapid hydrogen adsorption, may not be satisfied under certain conditions, and if this is the case, the effect will be evident in the subsequent kinetic analysis. This leads to the following simplified reaction sequence:

$$2\,M + H_2 \leftrightarrow 2\,M\text{-}H$$

$$M + CO \rightarrow M\text{-}CO$$

$$M\text{-}CO + M\text{-}H \rightarrow M\text{-}CH + M\text{-}O$$

$$M\text{-}O + 2\,M\text{-}H \rightarrow H_2O + 3\,M$$

$$M\text{-}CH + M\text{-}H \rightarrow M\text{-}CH_2 \rightarrow\rightarrow CH_4$$

with the common assumption that the rate-limiting step is the hydrogenation of surface carbon species:

$$M\text{-}CO + M\text{-}H \rightarrow M\text{-}CH + M\text{-}O$$

in which the series of reactions leading to methane are assumed to occur at the same rate under the steady-state approximation. The rate of reaction may then be written as:

$$rate = k\,\theta_H\,\theta_{CO} \tag{3}$$

where k is the intrinsic rate constant of the surface reaction and θ_i is the surface coverage of hydrogen or carbon monoxide. This result is quite similar to a simplified reaction sequence for methanation, reflective of the overall kinetics of the reaction, derived by Biloen and Sachtler [3]. As the authors note, their model is identical to that of Vannice [15] if it is assumed that C_{ads}, instead of $CHOH_{ads}$, is the dominant intermediate on the surface. Goodwin *et. al.* [25] also presents a similar mechanism for methanation over Ru/SiO_2.

For dissociative hydrogen adsorption, the hydrogen coverage is given by:

$$\theta_H = \frac{(K_H P_H)^{1/2}}{1+(K_H P_H)^{1/2} + K_{CO} P_{CO}} \tag{4}$$

where K_i is the steady-state equilibrium constant for either hydrogen or carbon monoxide, and P_i is the partial pressure of the same species. For molecular adsorption of carbon monoxide, the coverage is:

$$\theta_{CO} = \frac{K_{CO} P_{CO}}{1+(K_H P_H)^{1/2} + K_{CO} P_{CO}} \tag{5}$$

Equation 3 can now be expressed in terms of the equilibrium constants and partial pressures of the reactants:

$$rate = \frac{k(K_H P_H)^{1/2} K_{CO} P_{CO}}{\left[1+(K_H P_H)^{1/2} + K_{CO} P_{CO}\right]^2} \tag{6}$$

Note that although the derivation of equation 6 has resulted in the loss of parameters that are specific to this "microkinetic" model (such as the surface species coverages in equation 3), both forms of the rate equation, equation 3 and equation 6, will be utilized in the interpretation of results. Also, the fact that equation 6 contains the equilibrium constant for hydrogen adsorption allows for alterations in the second assumption for rapid hydrogen adsorption compared to product formation. Therefore, any changes in the kinetics of hydrogen adsorption will be manifested in the equilibrium constant and quantities related to it.

3.1.3 Transition State Theory

In processes where the kinetics of adsorption may influence reaction rates, transition state theory (TST) can be used to show the relationship between observed, or apparent, activation energies and heats of adsoprtion of reactants. The use of transition state theory is necessary in order to relate properties of the transition state activated complex, such as the activation energy, with rate parameters for the overall process.

According to TST, the rate constant k for a reaction can be expressed in terms of a pseudo equilibrium constant, K'', between the reacting species and the transition state activated complex [26]:

$$k = k_{barrier} \cdot K'' \tag{7}$$

where $k_{barrier}$, the number of transition state molecules reacting per unit time, is defined as:

$$k_{barrier} = \frac{k'T}{h} \tag{8}$$

where k' and h are Boltzmann's and Planck's constants, respectively and T is the absolute temperature. The pseudo equilibrium constant, K'', is related to the usual thermodynamic state functions by:

$$\Delta G^\circ = -RT \ln K'' = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where the thermodynamic variables represent the difference of the state functions between the activated complex and reactants referenced to a particular, common ground state. Equation (7) can now be expressed as:

$$k = \frac{k'T}{h} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H^\circ}{RT}\right) \tag{10}$$

Differentiation of the logarithm of this equation at constant pressure defines the activation energy, E_a, for the process under consideration and yields the following expression [26]:

$$\begin{aligned}\left(\frac{\partial \ln k}{\partial T}\right)_P &\equiv \frac{E_a}{RT^2} \\ &= \frac{\Delta H^\circ + RT}{RT^2}\end{aligned} \tag{11}$$

Therefore, $E_a = \Delta H^\circ + RT$, and:

$$k = \left[\frac{ek'T}{h} \exp\left(\frac{\Delta S^\circ}{R}\right)\right] \exp\left(-\frac{E_a}{RT}\right) \tag{12}$$

The utility of this result for the interpretation of the kinetic data from this study will be made clear in later sections. See Amdur and Hammes [26], Moulijn [27] and Boudart [28] for more lengthy discussions and detailed derivations.

3.2 Adsorption of Carbon Monoxide

As mentioned earlier, the key to many of the differences seen in catalyst activities and product distributions during FTS is believed to stem from the adsorption and dissociation behavior of carbon monoxide on the surface. While the kinetics of this process are not important to this study, knowledge of the mechanism and resulting carbon-to-metal ratio is necessary for the kinetic analysis.

Carbon monoxide can adsorb onto metal surfaces in a variety of configurations, but in general the carbon atom bonds to metal surface with the C-O bond perpendicular to the surface [29]. Dissociative chemisorption occurs on metals which can assist electron donation into the CO 2-π^* antibonding orbital [8] (back-bonding), so whether CO adsorbs molecularly or dissociatively depends on the location of the metal of interest on the periodic table [14] and on the temperature of the metal surface. Metals on which CO is typically dissociatively adsorbed include Fe, Ru, Co [30-32], while CO is molecularly adsorbed on Os, Ir, Pd and Pt [14, 20]. Depending on conditions, both types of adsorption can occur on Rh and Ni [33-34]. Regardless of the form in which the surface carbon exists, hydrogenation can occur with both species. It was the results of UPS and XPS studies [35] which showed that CO dissociation can occur on most transition metals that first led to the proposal of carbidic intermediates during FTS by Joyner [36] in 1977.

Catalytic activity is higher on surfaces where CO dissociates, as evident from the activity series of Vannice [15] presented earlier. Thus, it should not be surprising that CO adsorption on ruthenium is quite strong, and occurs molecularly only at temperatures near and below 300 K [4]. Linear and/or multiple-bonded forms of adsorbed CO exist, resulting in values of the number of CO molecules per metal atom from 0.4 to 2.3 [37, 38]. Bridge-bonded CO is more likely to rupture than linear CO because the linear M-C-O bond must be deformed more for the O atom to interact with the surface [39]. Gem-dicarbonyl (C:M = 2:1) and other multicarbonyls (C:M = 2:1 to 3:1) have also been identified on dispersed particles, but their existence is not necessary for dissociation, since this is known to occur on single crystal surfaces [14]. Thus, for adsorption on ruthenium at room temperature, it is likely that linear species are predominant, with a 1:1 Ru-to-CO ratio. Recently, Gupta [40] also reported a 1:1 ratio over Ru/TiO_2 catalysts.

Somorjai [14] lists several other factors which are important experimental considerations for this study: first, it is not known what type of bonding site is likely to lead to dissociation during reaction conditions; for the more active metals at 300 K and higher, CO desorbs from some crystal faces and dissociates on others; and activated carbon species can deposit as unreactive graphite above 700 K. Also, Yamada and Tamaru [41] have reported desorption of CO from Ru (0001) and Ru (21122) single crystal surfaces around 480K.

3.3 Adsorption of Hydrogen

The adsorption of hydrogen on ruthenium at low pressures has been a subject of considerable research [42], while several higher pressure studies have been conducted by our research group [43-52]. The dissociative adsorption of hydrogen usually occurs in a 1:1 metal-to-hydrogen ratio, although ^{1}H-NMR results have revealed that coverages far in excess of this value are common on ruthenium catalysts at higher pressures [43]. Two types of chemisorbed hydrogen have been identified by FTIR [53] and ^{1}H-NMR [49], and are referred to as weakly (or reversibly) and strongly (or irreversibly) bound hydrogen. The weakly bound hydrogen is known to exchange rapidly with the gas phase and the support [43], and to be highly mobile [44]. There is believed to be a stronger interaction between adsorbed hydrogen and low-coordination edge and corner "defect-like" sites on ruthenium particles, and the weakly bound hydrogen was found to be at least partially associated with these sites [49]. In addition, spillover to the support has been found to be substantial at higher pressures [48].

3.4 Coadsorption of Hydrogen and Carbon Monoxide

When hydrogen and carbon monoxide are either coadsorbed or sequentially adsorbed onto a surface, the following general phenomena have been noted [27]:

1. displacement of adsorbed H by CO;
2. blocking of H adsorption by preadsorbed CO;
3. segregation of adsorbed H and CO;
4. formation of mixed layers of adsorbed H and CO;
5. decrease in the desorption temperature of H; and
6. enhancement of CO uptake by preadsorbed H.

Recently, several of these observations have been confirmed for polycrystalline Ru and Ru/TiO_2 by Gupta and coworkers [40, 54-55], with coadsorbed CO and H_2 occurring on distinct Ru sites in a 1:1 ratio. The interaction of adsorbed CO and H on ruthenium is facilitated by empty, low-lying *d* valence orbitals, a condition which also favors CO dissociation. For these reasons, the reactivity of Ru towards FTS should not be surprising.