CHAPTER 7

MECHANISTIC IMPLICATIONS OF THE CHEMISORPTION OF CO AND H_2 IN THE FISCHER TROPSCH SYNTHESIS

The chemisorption of CO and H_2 by transition metals is a fundamental step in the production of hydrocarbons and oxygenates by the Fischer-Tropsch synthesis (FTS) and the methanation reaction (VII-1 - VII-7). A clear understanding of the nature of chemisorbed CO and H_2 can lead to an understanding of the mechanism of the hydrogenation of CO. This has spawned countless research efforts in this area. Herein will be reviewed a few of the most relevant works.

Chemisorption of H_2

The chemisorption of H_2 on transition metals is much simpler than CO chemisorption so not much emphasis will be placed on it for now. Dihydrogen is almost always adsorbed dissociatively on transition metals (VII-6,VII-8). The dipole moment is small for adsorbed hydrogen indicating that the M-H bond is covalent (VII-9); however, some studies indicate that the hydrogen species are hydridic (VII-10). Flash desorption experiments have shown that on most transition metals adsorbed hydrogen can exist in several states which are temperature and coverage dependent. Typically desorption experiments conducted on transition metals which have been exposed to low levels of H_2 show only one peak, thereby indicating the presence of only one adsorbed state. Increases in the amount of H_2 exposure to the metal surface usually result in complex desorption spectra with several peaks which desorb at lower temperatures with increasing hydrogen exposure. This indicates the presence of several states of adsorbed hydrogen. In the case of a polycrystalline Ni surface, two states have been identified which desorb at 380 K (β_2 state) and 310 K (β_1 state) where the β_2 state is filled before the β_1 state is formed (VII-11). Similar results have been reported for polycrystalline Fe surfaces. Wedler et al. identified a β_2 state which desorbed at 430 K and a β_1 state which desorbed at 350 K (VII-12). In addition they identified a γ state which desorbs at 90 K. This γ state was found only for surface coverages greater than monolayer and was identified as physisorbed hydrogen. Dus and Lisowski identified three states of hydrogen adsorbed on a Co film at 78 K which desorb at 360 K, 200 K and 90 K (VII-13). By measuring the surface potential changes, they were able to identify the species which desorbs at 360 K as electronegative atomic hydrogen, designated β^-. The state that desorbed at 200 K was identified as electropositive atomic hydrogen (β^+) and the state which desorbed at 90 K was identified as electropositive, molecularly adsorbed hydrogen (α). A second electronegative state which was believed to be associated with the β^- state was also observed in the desorption experiments as a shoulder to the β^- peak; this state was designated β_s^-. The appearance of different states has been proposed to arise form "a-priori" and "induced" heterogeneity (VII-9,VII-12). The "a-priori" heterogeneity could be caused by "sequential adsorption on different crystallographic planes" and the induced heterogeneity could be caused by repulsive lateral interactions which can cause restructuring of the hydrogen atoms at different coverages, as proposed by Wedler (VII-12).

Ertl has studied the adsorption of hydrogen on iron surfaces in order to better understand the kinetics of the ammonia synthesis (VII-9); however, much of his work can be related to the FT synthesis. He found that in the case of the Fe(110), Fe(100) and Fe(111) surfaces, hydrogen binds dissociatively with initial sticking coefficients of 0.1 up to 0.2. The initial heats of adsorption on these surfaces ranged from 21 to 26 kcal/mol which are close to the value of about 23 kcal/mol obtained by Wedler et al. on polycrystalline iron films. Ertl found that the adsorption energies on all 3 surfaces decreased with decreasing coverage. In addition, he determined that the Fe-H bond strength is on the order of 60-65 kcal/mol. TDS experiments verified that above 200°C, temperatures at which the FTS takes place, the desorption of hydrogen is very rapid and an "adsorption-desorption equilibrium for hydrogen will always be established.

Chemisorption of CO

CO is attached to metals through the carbon atom, as in nearly all carbonyl compounds. On low index planes the molecular axis is nearly perpendicular to the surface while with more open planes the ligand may be tilted in order to maximize orbital overlap. In rare instances, there is evidence of CO lying flat on a metal surface, e.g., the 311 surface of Cu (VII-14).

The bonding of CO chemisorbed on transition metals is much like that of metal carbonyls (VII-14a) and is usually described in terms of the Blyholder Model (VII-15). Overlap of the filled 5σ orbital on the carbon with a d_z2 and s orbital of the transition metal forms the first. Overlap of an empty antibonding $p\pi$ ($2\pi^*$) orbital of CO with a filled $d\pi$ or $dp\pi$ (d_{xy} or d_{yz}) metal orbital forms the second. The accumulation of electron density on the metal due to electron flow from the carbon to metal via the σ bond is relieved by back donation of electron density into the antibonding $p\pi$ orbital of CO. The back bonding makes the CO molecule negative, increasing its basicity, while simultaneously the flow of electrons from the CO to the metal helps to make the CO positive. This type of bonding is synergic since the formation of the M-C σ bond strengthens the M-C π bond and vice versa. However, the electron density due to the back donation is located in the antibonding pπ orbital of CO. As the M-C bond strength increases, the C-O triple bond becomes weaker. This is reflected by a decrease in the vibrational frequency of the C-O bond when CO is chemisorbed.

In contrast to the 5σ and the $2\pi^*$ orbitals of CO, the 4σ and 1π orbitals are only slightly involved in the chemisorption of CO (VII-16 - VII-18). The 4σ and 1π orbitals are both bonding in terms of the carbon and oxygen of the CO molecule; however, back bonding from a transition metal into the $2\pi^*$ orbital increases the carbon-oxygen separation. The increasing of the carbon-oxygen separation decreases the orbital overlap which in turn decreases the bonding character and increases the energy of the 4σ and 1π orbitals. Since the 1π orbital is more bonding than the 4σ orbital, the increase in energy is different for both orbitals. The total increase in the energy separation of the two orbitals is given as $\Delta(1\pi\text{-}4\sigma)$. For chemisorbed CO, the value $\Delta(1\pi\text{-}4\sigma)$ ranges from 2.6 to 3.0 eV as compared to 2.75 eV for free CO.

Brodén et al. found that $\Delta(1\pi\text{-}4\sigma)$ changes systematically for M-CO Å in relation to the position of M on the periodic table (VII-18). The value of $\Delta(1\pi\text{-}4\sigma)$ increases moving from right to left on each row and increases going up each column. Based on the arguments for the energy separation, $\Delta(1\pi\text{-}4\sigma)$, the C-O stretching increases from right to left along a row and from bottom to top along a column. It was observed that the tendency of a metal to dissociate CO also follows this same trend. All of the metals which dissociate CO at room temperature lie to the left of Co, Ru and Re

(Figure VII-1). This, according to Brodén et al., "establishes a direct correlation between dissociation and geometric stretching" of the C-O bond. "The larger the tendency to dissociate, *i.e.*, the smaller the activation energy barrier for dissociation, the larger the value of $\Delta(1\pi\text{-}4\sigma)$." According to Brodén et al., the value of $\Delta(1\pi\text{-}4\sigma)$ does not depend on the surface structure of the metal. The electronic properties of the metal play the most important role in chemisorption of CO and the surface geometry is secondary. However, for metals on the borderline between dissociation and molecular chemisorption of CO, i.e., W, the surface geometry can be the deciding factor of the type of chemisorption. For example, CO is dissociatively adsorbed on W(100) and molecularly adsorbed on W(110).

Sung and Hoffman have performed extended Huckel calculations and identified the same trend discovered by Brodén et al. (VII-19). They found that the metal d orbitals become very diffuse moving right to left across the periodic table. This in turn causes the CO $2\pi^*$ orbital to obtain more electron density, thus weakening the C-O bond. In addition, they found that the site of adsorption on a metal surface had little effect on dissociation as compared to which metal the CO was adsorbed.

Benzinger has investigated the thermodynamics of adsorption of CO on transition metals and has also obtained results very similar to Brodén (VII-20). According to Benzinger the chemisorption of diatomic molecules can be described as a competition between molecular and dissociative adsorption.

$$AB_{(g)} \leftrightarrow AB_{ads}$$

$$AB_{ads} \leftrightarrow A_{ads} + B_{ads}$$

The fractional coverages of molecular and dissociated adsorbed species are given as:

$$\theta_m = K_m P / (1 + 2K_D^{1/2} P^{1/2} + K_m P)$$
$$\theta_D = K_D^{1/2} P^{1/2} / (1 + 2K_D^{1/2} P^{1/2} + K_m P) \qquad \text{[VII-1]}$$

The equilibrium constants, K_m and K_D are defined as:

$$K_m = \left(\frac{h^2}{2\pi mkT}\right)^{3/2} \frac{1}{kT} \frac{f'_{a,m}}{f'_g} \exp\left(\frac{\epsilon_m}{kT}\right)$$
$$\text{and} \qquad \text{[VII-2]}$$
$$K_D = \left(\frac{h^2}{2\pi mkT}\right)^{3/2} \frac{1}{kT} \frac{f'_{a,D}}{f'_g} \exp\left(\frac{\epsilon_D}{kT}\right)$$

where $f'_{a,m}$ and $f'_{a,D}$ are partition functions for internal degrees of freedom and ϵ_m and ϵ_D are the energies given off during molecular and dissociative adsorption at 0 K. For molecular and dissociative adsorption, the internal partition function is essentially 0 and for free gas molecules the only significant contribution to the internal degrees of freedom are rotational degrees of freedom. These simplifications give:

$$\frac{f'_{a,m}}{f'_g} = \frac{f'_{a,D}}{f'_g} = \frac{\theta_r}{T} = \frac{2.5}{T} \qquad \text{[VII-3]}$$

where θ_r is the rotational temperature (for diatomic molecules θ_r=2-3 K). Benzinger further assumed that the heat of adsorption is equal to the zero temperature adsorption energy,

$$\epsilon_m = -\Delta H_{ad,m} \text{ and } \epsilon_D = -\Delta H_{ad,D} \qquad \text{[VII-3]}$$

which gives the following expressions for K_m and K_D,

According to equation 4, at low temperatures, molecular adsorption is dominant since the surface can adsorb twice as many molecules as dissociated species. At higher temperatures, entropy plays an important role. The entropy change for adsorption of

$$K_m=\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\frac{1}{kT}\,\frac{2.5}{T}\exp\left(\frac{-\Delta H_{ad,m}}{kT}\right)$$
and
$$K_D=\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\frac{1}{kT}\,\frac{2.5}{T}\exp\left(\frac{-\Delta H_{ad,D}}{kT}\right) \qquad \text{[VII-4]}$$

both molecular and dissociated species is ~200 J/g-mol·K. Since dissociative adsorption results in half as many molecules being adsorbed as molecular adsorption, the entropy change per site is less for dissociative adsorption. As shown in Figure VII-2, when $\Delta H_{ad,m}=125$ and $\Delta H_{ad,D}=135$ kJ/mol, and $P=10^{-8}$ torr, at temperatures below 250K only molecular adsorption takes place. However, between 250 and 325K substantial dissociative adsorption takes place. Above 400K essentially no adsorption takes place. From the above relationships, it can be seen that as the enthalpy of molecular adsorption becomes more exothermic than the enthalpy of dissociative adsorption, the amount of dissociative adsorption decreases. Pressure also has a major effect on the nature of the chemisorption. When pressure is increased at constant temperature, molecular adsorption becomes more favored. This can be seen from equation 1 where θ_m/θ_D is proportional to $P^{1/2}$.

In order to determine whether or not CO, N_2 and NO will undergo dissociative chemisorption, the heats of molecular and dissociative adsorption need to be known. On metals where only molecular adsorption takes place, $\Delta H_{ad,m}$ can be experimentally determined. In other cases the heats of molecular adsorption are approximated by the activation energy of desorption. The heats of dissociative adsorption must be approximated. Benzinger has proposed that since CO, N_2 and NO dissociate into surface carbides, nitrides and oxides, the heat of dissociative adsorption is close to the enthalpy difference between the gas phase molecule and the heats of formation of the metal carbides, nitrides and oxides.

$$\Delta H_{ad,D}(CO)=\Delta H_f(MC) + \Delta H_f(MO) - \Delta H_f(CO_{(g)}),$$

$$\Delta H_{ad,D}(NO)=\Delta H_f(MN) + \Delta H_f(MO) - \Delta H_f(NO_{(g)})$$

$$\Delta H_{ad,D}(N_2)=2\Delta H_f(MN) - \Delta H_f(N_{2(g)})$$

According to Benzinger, dissociation will occur to a significant amount when θ_D and θ_m are approximately equal.

$$\theta_D/\theta_m \approx 1 . \qquad [VII-5]$$

Relating equations 2 and 4 with equation 5 gives the following expression:

$$2\epsilon_m - \epsilon_D = -kTln\left\{\left(\frac{h^2}{2\pi mk}\right)^{3/2} \frac{\theta_r}{k} \frac{P}{T^{7/2}}\right\} \qquad [VII-6]$$

The total surface coverage of dissociated and molecular species is approximately unity when $\epsilon_m = \epsilon_D$. From Benzinger's work it is clear that if the heat of dissociative adsorption is 10 kJ/mol greater than the heat of molecular adsorption then molecular adsorption will dominate. By setting a lower limit of -170 kJ/mol for molecular adsorption, Benzinger has proposed that metals to the left of Fe, Tc and W must dissociate CO at room temperature. In the cases where the calculated values of the heat of molecular adsorption are less than the heat of dissociative adsorption, no CO dissociation takes place. Benzinger's results give a thermodynamic explanation for the experimental results of Brodén.

In the case of N_2, the heat of molecular adsorption is expected to be small (~20 kJ/mol) for all transition metals. This indicates that the only requirement for N_2

dissociation is that the heat of dissociation be exothermic. This is the case for all metals to the left of Fe, Tc and W just as Brodén reported.

Miyazaki, utilizing the Bond Energy Bond Order (BEBO) model has investigated the nature of chemisorption of N_2, H_2 and CO on transition metals (VII-8). In this model, a diatomic molecule, AB, first binds molecularly to the metal surface, M_s.

$$M_s + A\text{-}B \rightarrow M_s \cdots A \cdots B \cdots M_s \rightarrow M_s\text{-}A + M_s\text{-}B$$

and then dissociates to bound A and B species. The interaction energy between the molecule and the metal surface, V_{AB} is written as

$$V_{AB} = D_{AB} - E_{A\text{-}B,sur} - E_{M_s\text{-}A} - E_{M_s\text{-}B} \qquad \text{[VII-7]}$$

where D_{AB} is the dissociative energy of the diatomic molecule, $E_{A\text{-}B,\ sur}$ is the energy of the A-B bond of the molecule on the surface and $E_{M_S\text{-}A}$ and $E_{M_s\text{-}B}$ are the energies of the bonds between the metal surface and the dissociated species. For N_2 and CO, $E_{A\text{-}B,\ sur}$ is given by the following experimentally derived equations:

$$E_{N\text{-}N,sur} = 6.667n^3_{N\text{-}N} - 8n^2_{N\text{-}N} - 39.333n_{N\text{-}N}$$

and

$$E_{C\text{-}O,sur} = -13.333n^3_{C\text{-}O} + 56n^2_{C\text{-}O} + 37.334n_{C\text{-}O}$$

where n is the bond order of molecularly adsorbed N_2 or CO which ranges from 0 up to 3. In the case of H_2, the following equation was used:

$$E_{H\text{-}H,sur} = D_{H_2} n^{1.041}_{H\text{-}H}$$

Miyazaki assumed that the total bond energy between the adsorbed atoms and the metal surface, $E_{M_s\text{-}X}$ (X=A or B) is proportional to the bond order $n_{M_s\text{-}X}$.

$$E_{M_s\text{-}X} = E_{M_s\text{-}X,s} n_{M_s\text{-}X}$$

where $E_{M_s\text{-}X,s}$ is the single bond energy of the M_s-X bond. The total bond order of the dissociatively chemisorbed atomic species is given as:

$$n_{M_s\text{-}A} + n_{M_s\text{-}B} = \lambda(n^\circ_{A\text{-}B} - n_{A\text{-}B})$$

where $n^\bullet_{A\text{-}B}$ is the bond order of the free gas molecule (3 for N_2 and CO, 1 for H_2) and λ is "a constant representing the ratio of the forming bond order, $n_{M_S\text{-}A} + n_{M_S\text{-}B}$, to the losing bond order, $n^\bullet_{A\text{-}B}$-$n_{A\text{-}B}$ during the surface reaction." The value of $n_{A\text{-}B}$ is taken to be 0 since the molecule is dissociated. The values of $n_{M_S\text{-}A}$ and $n_{M_S\text{-}B}$ are taken to be those for the gas molecules A_2 and B_2 that is, $n_{M_S\text{-}O} = 2$ since $n_{O_2} = 2$ and $n_{M_S\text{-}C} = 3$ since $n_{C_2H_2} = 3$. Combining equations gives:

$$V_{AB} = D_{AB} - E_{A\text{-}B,sur} - \lambda E_{M_s\text{-}A,s}(n^\circ_{A\text{-}B} - n_{A\text{-}B}) + (E_{M_s\text{-}A,s} - E_{M_s\text{-}B,s}) n_{M_s\text{-}B} \qquad \text{[VII-8]}$$

for heteronuclear diatomic molecules and,

$$V_{AB} = D_{AB} - E_{A\text{-}B,sur} - \lambda E_{M_s\text{-}A,s}(n^\circ_{A\text{-}B} - n_{A\text{-}B}) \qquad \text{[VII-9]}$$

for homonuclear molecules. The values of $E_{M_s\text{-}A,s}$ and $E_{M_s\text{-}B,s}$ were evaluated in other works by Miyazaki. For the chemisorption of H_2 on transition metals, the interaction energy is given as:

$$V_{H_2} = 103.2(1 - n_{H-H}^{1.041}) - 2(1 - n_{H-H}) E_{M_s-H,s} \qquad [VII-10]$$

A plot of V_{H_2} vs. n_{H-H} ($1 \geq n_{H-H} \geq 0$) is shown in Figure VII-3. There is no maximum value or minimum value of V_{H_2} so there is no activation energy or potential well during the chemisorption of hydrogen. This indicates that hydrogen readily adsorbs to transition metals and dissociates.

The chemisorption of CO takes place in two steps:

$$M_s + CO \rightarrow M_s \equiv C\text{-}O \text{ for } 0 \leq n_{M_s-C} \leq 3 \text{ and } 3 \geq n_{C-O} \geq 1.2$$

and

$$M_s \equiv C\text{-}O + M_s \rightarrow M_s \equiv C + M_s = O \text{ for } 0 \leq n_{M_s-O} \leq 2 \text{ and } 1.2 \geq n_{C-O} \geq 0.$$

The value of 1.2 for n_{C-O} is the point where the bond is weakened enough for O to interact with the metal surface. The energies of these steps are given as

$$V_{CO} = 256 - E_{C-O,sur} - 1.667(3 - n_{C-O}) E_{M_s-C,s} \qquad [VII-11]$$

and

$$V_{CO} = 256 - E_{C-O,sur} - 3E_{M_s-C,s} - 1.667(1.2 - n_{C-O}) E_{M_s-O,s} \qquad [VII-12]$$

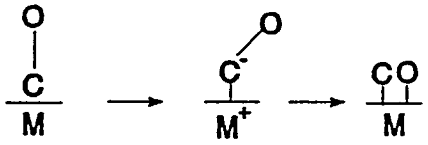
A plot of the results for these two equations versus bond order for a series of transition metals is shown in Figure VII-4. A potential well exists for most metals between n_{C-O}=2.5 and 2.0 (except for Hf, Ta, Zr, Nb and W). For these metals, molecular chemisorption can occur without any activation energy. In the cases of Pd, Rh, Pt , Ru Ir and Os, the Noble metals, the energy separation between the potential well of molecular adsorption and the activation energy of dissociation are so large that molecularly adsorbed CO is stable. In the cases of Co, Ni, Tc, Fe and Re the energy separation is much smaller and both molecular and dissociative chemisorption can occur simultaneously depending on the temperature and pressure etc. For the remaining metals Mo, Cr, Mn, Ti and V, dissociation is more likely than molecular adsorption because the energy difference is small or negligible. The results of Miyazaki are similar to the experimental results obtained by Brodén et al. In general, dissociative chemisorption is more likely moving to the left across a row and up a column on the periodic table. a break occurs at Fe, Tc and W where to the right molecular chemisorption is favored and to the left dissociative is favored.

In the case of nitrogen, the plot of the interaction energy of N_2 versus bond order for transition metals is shown in Figure VII-5. In general, there is an activation energy for nitrogen adsorption on all transition metals which decreases going to the left of the periodic table. Like hydrogen adsorption, there is no potential well, so there is no stable molecularly adsorbed N_2 state for any metal at room temperature. Dissociative chemisorption occurs at room temperature for Hf, Ta, Zr, Nb, Ti, Mn, V, W and Cr where the activation energy is < 20 kcal/mol. These results are also consistent with the findings of Brodén et al.

Brodén's experimental evidence has shown that CO is dissociatively adsorbed on first row transition metal surfaces from Sc to Fe but is molecularly adsorbed from Co to Cu. Pavão et al. have discussed the metal-CO charge transfer process of chemisorbed CO in terms of Pauling's resonating-valence-bond theory and *ab initio* molecular-orbital calculations (VII-21). They found from *ab initio* molecular orbital calculations that each metal from Sc to Fe is positively charged while it is essentially neutral from Co to Cu. According to Pavão et al., Pauling's resonating-valence-bond theory: "unsynchronized resonance of covalent bonds describes charged transport in metals by transferring a bond from one atom to the next, accompanied by the creation of M^+, M^0, and M^- states,

$$M - MM \rightarrow M^+M - M^-.''$$

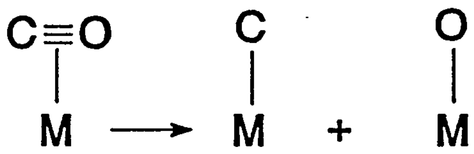
The atom which receives a bond must have an orbital available to receive it. In the case of the interaction between CO and a metal this orbital is the LUMO, $2\pi^*$, orbital of CO. For M-CO systems with net charge transfer the unsynchronized resonating-valence bond mechanism of CO dissociation is presented as



The first step of the dissociation involves the formation of a bond between CO and the metal surface. In the second step the C-O bond is transferred to the positively charged metal surface returning the surface to the 0 valence state and causing the rupture of the C-O bond.

Structure of Predissociative Intermediate

Rofer-Depoorter has proposed that CO is bound to a metal in a "side on" fashion before it is dissociated (VII-6). She states, "The side on CO must be the precursor to dissociation, because breaking of the C-O bond in end-on CO should lead to loss of the oxygen to the gas phase, which does not seem to occur." Instead the oxygen remains bound to the metal.



Moon et al., utilizing XPS and TPD have shown, for Fe(100), CO is molecularly chemisorbed in three sequential states designated α_1, α_2 and α_3 (VII-22). The thermal desorption spectra obtained by Moon et al. are shown in Figure VII-6. It is clear from the figure that as an Fe(100) surface is exposed to CO the α_3 state is filled first followed by the α_2 state and finally the α_1 state. After 12 L of CO exposure, saturation occurred and all three states were filled. According to the temperature of desorption, it is clear that the α_3 state is the most tightly bound state followed by α_2 and α_1 states. The activation energies for α_1, α_2 and α_3 states were determined to be 12.8, 18.0 and 26.2 kcal/mol respectively. A fourth state referred to as the β state is seen to desorb at 820K. This β state is believed to be formed by the recombination of C and O atoms from dissociated CO molecules. The α_3 state is believed to be the precursor to CO dissociation because CO exposures resulting in the saturation of the α_3 state also result in the saturation of the β state. An increase in the intensity of the α_1 and α_2 desorption peaks did not correspond to an increase of the β peak so it was inferred that α_1 and α_2 states desorb as molecular CO. The desorption peak corresponding to the α_3 state was slightly asymmetric so it is believed that the α_3 state desorbs molecularly as well as dissociatively. In support of the α_3 state being the precursor to CO dissociation it was found that at 498K the O(1s) binding energy of the CO is approximately 530 eV which is characteristic of chemisorbed $O^{\delta-}$.

In another study, Moon et al., utilizing high-resolution electron energy loss spectroscopy (HREELS), found the C-O stretching frequency of the α_1, α_2 and α_3

states are 2070, 2020 and 1210 cm^{-1} respectively (VII-23). The C-O stretching frequency of a free CO molecule is 2143 cm^{-1}. The stretching frequency of the α_1 and α_2 states are typical of linear metal carbonyl compounds; however, the stretching frequency of the α_3 state implies a weakening of the C-O bond which is consistent with the α_3 state being the precursor to CO dissociation.

Using near edge X-ray absorption fine structure (NEXAFS), Moon et al. were able to show that the CO molecule is tilted at an angle of $45^\circ \pm 10^\circ$ with respect to the metal surface in the α_3 state (VII-24). In addition it was found that the CO molecule is bound in the four fold hollow of the Fe(100) face in the α_3 state and that the C-O bond length is 0.07±0.02 Å longer in the α_3 state than it is in the α_1 and α_2 states. A more precise measure of the Fe-CO tilt angle has been made by Saiki et al. using combined polar and azimuthal X-ray photoelectron diffraction (VII-25). They found that the CO molecule is tilted $35^\circ \pm 2^\circ$ with respect to the surface. Assuming the CO molecule binds in the four-fold hollow point (Figure VII-7), then the C-Fe vertical distance has been determined to be either 0.2±0.1 or 0.6±0.2 Å.

Pavão et al., in a follow up to their study mentioned above, studied the interaction of CO with the Fe(100) surface using ab initio unrestricted-Hartree-Fock, effective-core potential and multiple-scattering Xα molecular-cluster calculations (VII-26). The Fe(100) surface was represented by a Fe_5CO cluster model in which the surface is depicted by four Fe atoms arranged in a square with sides of 2.87 Å. The fifth Fe atom is located below the surface, 2.48 Å from each of the surface Fe atoms. Of the five CO configurations studied, CO at 90°, 45° and 0° and with CO lying parallel and diagonally to the Fe_4, it was found that the CO bound 45° to the surface had the highest Fe→CO charged transfer and the lowest Fermi level. The results of MS Xα calculations of linear FeCO, end-on Fe_5CO (hollow), bent 45° Fe_5CO, and end-on Fe_5CO (deep hollow) indicate back donation of the linear FeCO and end on Fe_5CO are virtually the same while that of the bent Fe_5CO is much higher. The vibrational frequency of an absorbed CO molecule is inversely proportional to the back donation. The ratio of the back donation of the two perpendicular modes to the bent mode is 0.5 and the ratios of the frequencies of the α_1 and α_2 states to the α_3 state are 0.6. According to Pavão et al., this is a good indication that the α_3 state corresponds to bent CO while the α_1 and the α_2 states correspond to perpendicularly bound CO.

Effects of Alkali Promotion on the Chemisorption of CO and H_2

It is common knowledge that iron Fischer-Tropsch catalysts must be promoted with a small amount of an alkali salt in order to obtain a high molecular weight and olefinic product (VII-27 - VII-30). The alkali metals, Na, K, Rb and Cs are the best promoters; however, Li is considered to have no value as a promoter. In practice, K is used predominantly due to a compromise between cost and effectiveness.

Dry et al. have investigated the effect of K on the heats of chemisorption of CO, H_2 and CO_2 on unsupported and supported reduced Fe_3O_4 catalysts (VII-31). The heats of CO adsorption on Fe_3O_4, Fe_3O_4 + 1.6% MgO, Fe_3O_4 + 1.6% MgO + 0.38% K_2O, Fe_3O_4 + 1.6% MgO + 1.06% K_2O, and Fe_3O_4 + 1.6% MgO + 0.1% Li_2O, range between 32 and 27 kcal/mol at low coverage (θ<0.1). The unpromoted and MgO promoted Fe_3O_4 had essentially the same heats of adsorption, thus indicating that MgO is a structural promoter and not an electronic promoter. The heats of adsorption of the K_2O promoted Fe_3O_4 were substantially higher than those containing no K_2O;

however, the Li_2O promoted sample had a heat of adsorption lower than that of the unpromoted Fe_3O_4. At low coverages the heats of hydrogen adsorption on these samples were found to be opposite in magnitude to those of the heats of CO adsorption. The K_2O promoted samples gave the lowest heats of adsorption while the Li_2O promoted sample had the highest heats of adsorption. The heat of CO_2 adsorption on the 0.38% K_2O promoted Fe_3O_4 was found to be the highest of the samples studied. The unpromoted and 1.6% MgO samples had virtually the same heats of CO_2 adsorption. The presence of K_2O is known to increase the ability of Fe catalysts to adsorb CO_2 so these results were not surprising to Dry.

To verify K_2O inhibits hydrogen adsorption, Dry performed CO chemisorption studies on hydrogen presorbed iron samples. When CO was allowed to chemisorb on a hydrogen presorbed sample that had been evacuated, the CO coverage was less than half of what it had been on a clean sample. When the same experiment was performed on a K_2O promoted sample the CO coverage and heat of CO adsorption were the same as when a clean iron sample was used. Dry reasoned that K_2O weakens the Fe-H bond thereby making it easy for hydrogen to be stripped off the metal surface under vacuum, thus making sites available for CO adsorption. Similar results were obtained by Arakawa and Bell (VII-28). In the case of the unpromoted iron, some hydrogen remained bound to the surface of the iron which decreased the number of binding sites available for CO. Dry et al. also found that twice as much CO was adsorbed as hydrogen at low pressures. This seemed to indicate that CO was bound molecularly in a linear fashion while hydrogen was adsorbed dissociatively. Benzinger and Madix obtained different results for the effect of K promotion on the adsorption of hydrogen on iron. They found the sticking probability and the binding energy of hydrogen increases with K promotion (VII-32). It was suggested that the difference in the results came about because Dry et al. may not have used clean iron surfaces for their studies since the heats of adsorption of H_2 were similar to the heats of adsorption of H_2 on iron oxide.

Dry *et al.* interpreted their results in terms of the Fischer-Tropsch synthesis in the following manner. When CO adsorbs on transition metals it accepts electrons from the metal surface ($M \rightarrow p\pi^*$). Potassium is a Lewis base so it donates electrons to the metal which can then flow into the $2\pi^*$ orbital of CO. This phenomenon helps the adsorption of CO and increases the strength of the M-CO bond. Several studies have shown that at moderate coverages, hydrogen adsorbed to a metal surface will donate electrons to the metal. In this case the electron donating properties of K decrease the ability of hydrogen to chemisorb. The ability of K promoted catalysts to produce an olefinic product can then be explained in terms of a decrease of hydrogen chemisorbed on the catalyst which in turn decreases the hydrogenation activity of the catalyst. At the time of Dry's work, it was believed that the FT synthesis proceeded through a surface hydroxyl intermediate, $HCOH_{ads}$, which was bound to the metal by the carbon atom. Dry believed that the K weakened the C-O bond of adsorbed carbon monoxide making it susceptible to attack by hydrogen thereby producing the hydroxyl intermediate. In addition, the strengthening of the M-C bond by K increases the residence time of the intermediate on the catalyst which increases the probability of chain growth. A current theory has a surface carbide species as being the intermediate responsible for chain growth (this is discussed in more detail later). In an analogous fashion, K would increase the rate of dissociation of CO by assisting in the weakening of the C-O bond. The resulting surface carbide would then be hydrogenated and polymerized. The enhancement of the CO dissociation would result in an increase in the amount of surface carbide species available for polymerization, and would result in a higher molecular weight product than would be obtained without K. Similarly Benzinger and Maddix proposed that the enhanced dissociative chemisorption of CO on K promoted iron comes about by an interaction between the K(4s) and CO($2\pi^*$) states (VII-32). They explained this phenomenon as follows: "The coupling between the K(4s) state and a CO($2\pi^*$) state caused the bonding MO formed between these states and an Fe(3d) state to be pushed to lower energy and increase the adsorption bond strength." This in turn may lead to dissociation of the adsorbed CO.

According to McClory and Gonzalez, alkali promotion of FT and methanation catalysts should increase the activity of the catalysts if alkali metals promote the dissociation of CO; however, the opposite effect is generally observed (VII-33). Since surface carbon is formed by the dissociation of CO, carbon buildup will come about as the result of either an increase in the CO dissociation or a decrease in the hydrogenation of surface carbon. As they point out, alkali promotion increases the rate of carbon buildup. It is their opinion that since this increase in carbon buildup depresses the rate of methanation more than it does the rate of formation of higher carbon number hydrocarbons, alkali promotion is actually the result of selective poisoning. They studied a series of Li, Na, K and Cs promoted Ru catalysts supported on SiO_2. At constant temperature (220°C) the olefin selectivity was very poor for the unpromoted catalysts but increased greatly for the Cs and K promoted catalysts. In addition, there was a marked increase in the amount of higher molecular weight products for the alkali promoted catalysts compared to the unpromoted catalysts. When these catalysts were run under conditions so that the CH_4 turnover rate or the CO conversion was essentially identical for all of the catalysts there was very little difference in the olefin selectivity or the amount of high molecular weight products for the unpromoted and promoted catalysts. Temperature programmed desorption studies (TPD) were performed on the catalysts to see what effect alkali promotion has on CO adsorption. Three peaks were observed at 100, 220, and 450°C. the intensity of the peak at 220°C was found to increase upon the addition of alkali promoters. This was interpreted as a slight increase in the binding strength of CO for the promoted catalysts. The peak at 450°C was determined to be from the loss of CO_2 due to the reaction of H_2O from the support and surface carbon on the catalyst. Since the area under this peak was identical for all catalysts it was determined that alkali did not effect the amount of surface carbon. IR spectroscopy showed that addition of alkali caused the CO stretching frequency of adsorbed CO to decrease from 2038 cm^{-1} to about 2036 cm^{-1} for Li, all the way to 2018 cm^{-1} for Cs. This red shift indicates a weakening of the C-O bond; however, they point out that if alkali causes a weakening of the C-O bond, then it should increase the rate of CO dissociation and subsequently the rate of formation of surface carbon. Since they found no such increase in surface carbon when CO conversions were held constant, it was concluded that the increase in carbon formation for alkali promoted catalysts under reaction conditions (constant temperature) must be due to a decrease of the rate of hydrogenation of the surface carbon. The presence of alkali depresses the rate of CH_4 formation because it is "more hydrogen demanding than the Fischer-Tropsch reaction." Since the hydrogenation step is hindered by alkali, less CH_4 and less paraffins are formed. According to McClory and Gonzalez, there are two possibilities: (1) the alkali reduces the availability of H_2 on the surface or (2) alkali modifies the rate at which H_2 adds to the surface carbon as the result of an ensemble effect (VII-33). They believe that an electronic effect is secondary to that of an ensemble effect caused by site blocking of Ru ensembles by the alkali atoms. The hydrogenation step is; therefore, "more sensitive to the size of the ensemble and to the manner in which carbon is bound to the surface than to the dissociation of CO."

The kinetics of formation of primary hydrocarbon products and secondary reactions such as hydrogenation and double bond isomerization of 1-alkenes were studied by Herzog and Gaube using unpromoted and alkali promoted iron catalysts (VII-34). The reaction order of hydrocarbon formation, hydrogenation and isomerization with respect to H_2 were found to be 1,1 and 0 respectively for promoted and unpromoted catalysts. With respect to CO, these reaction orders were found to be 0, -2, and -2 respectively for both promoted and unpromoted catalysts. Alkali promoters have no effect on the orders of these reactions. The reaction rate of hydrogenation can then be given as:

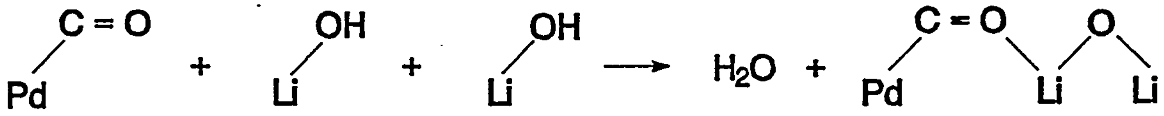
$$r_1 = k_1' P_{H_2} \frac{C_{1-en}}{P_{CO}^2} \qquad \text{[VII-13]}$$

where P_{H_2} and P_{CO} are the partial pressures of H_2 and CO respectively and C_{1-en} is the concentration of 1-olefins. The increase in olefin selectivity for alkali promoted catalysts can then be explained by either an increase in the rate of adsorption of CO which reversibly deactivates the catalyst or a decrease in k_i due to a reduction of hydrogenation capacity of the alkali promoted catalyst.

The hydrogenation activity of 1-hexene by a Cs_2CO_3 promoted iron catalyst was studied in order to answer the question raised above. The hydrogenation capacity of the Cs promoted and unpromoted catalysts were found to be essentially the same with about 90% of the 1-hexene converted to hexane. The reaction order of 1-hexene hydrogenation and isomerization to 2-hexene were found to be ~1.5 which was close to that found for olefins in the FT experiments. When the hydrogenation of 1-hexene was carried out in the presence of a small amount of CO, the hydrogenation capacity of the alkalized catalysts decreased dramatically relative to the unpromoted catalyst. In addition, the degree of isomerization of 1-hexene to 2- hexene decreased as well. It was concluded that alkali increases the strength of CO adsorption which causes 1-alkenes to desorb at a higher rate than for unpromoted catalysts. This in turn decreases the amount of alkenes hydrogenated and isomerized.

Pitchon et al. have studied the effects alkali promotion has on the chemisorption of CO on a SiO_2 supported Pd catalyst (VII-35). The promotion of Pd with alkali metals increases its activity and selectivity during the methanol synthesis. From vibrational spectroscopy, it has been deduced that alkali promoters cause a decrease in the υCO frequency by either donating electrons to the metal surface or through interactions between the alkali metal and the oxygen of the adsorbed CO.

IR spectroscopy of CO chemisorbed on 1.5 wt.% Pd/SiO_2 shows three bands at 2088 cm^{-1}, 1965 cm^{-1}, and 1910 cm^{-1} corresponding to linearly bound CO, bridging CO on the Pd(100) face and bridging CO on the Pd(111) face respectively. The positions of these bands are dependent with the peaks shifting to low frequencies with lower CO pressures. The catalysts promoted with Na, K and Cs show the same three bands; however, a fourth band is also observed at lower frequencies (~1875 cm^{-1}) and is referred to as the "I" band. It was found that for either Na or K as the reduction temperature of the catalyst was increased from 573K to 673K, the intensities of the L, B_1 and B_2 bands decreased while the I band shifted to lower frequencies. This was interpreted as meaning that as the reduction temperature increases, the CO chemisorption is more affected by the alkali. Pitchon et al. had seen in another study that as the reduction temperature increases the alkali becomes more uniformly distributed over the SiO_2 and the Pd catalyst (VII-36). It was also found that an increase in the alkali promoter content for a given reduction temperature causes the L, B_1 and B_2 bands to decrease and the I band to shift to lower frequency (VII-35). It was reasoned that these results indicate a strong interaction between the promoter and the adsorbed CO. In addition it was found that the I band is shifted to lower frequencies upon going from Cs to K to Na. This effect is the opposite expected if electron donation from the alkali to metal were the cause of the C-O weakening. Pitchon et al. have proposed that the effect observed in this study was due to CO bound to the metal via the carbon atom and to an alkali atom via the oxygen atom. This type of interaction has been shown to produce a decrease in υCO bands in organometallic molecules (VII-37 - VII-39). In these studies it was found that the υCO band shifts to lower frequencies are larger for alkali with smaller ionic radii (higher electrostatic fields). Pitchon et al. pointed out that for the molecule $CpCo(CO)_3$ -M^+ where M^+=Li, Na or K, the CO stretching frequencies are 1717, 1743 and 1748 cm^{-1} respectively. This type of interaction has been proposed for Ni and Pd catalysts as well (VII-40,VII-41). The case of Li is much more complex and it has not been placed in the trends Na>K>Cs. In the case of Li, water is formed during the chemisorption of CO.



The adsorbed water shows an IR band at 1625 cm^{-1} which grows in as the I band grows at 1820 cm^{-1}. The I band in the case of Li does not follow the trend, but Li is known to be the most active alkali promoter for the methanol synthesis.

Since N_2 is isoelectronic with CO, it is of interest to examine the effects of K on the chemisorption of N_2. It has been determined that the rate-limiting step of the ammonia synthesis is the dissociative adsorption of N_2 (VII-9). The presence of a small amount of K on the surface of industrial catalysts is known to increase the activity of the catalysts (VII-42); therefore, K must increase the rate of dissociative adsorption of N_2 (VII-9,VII-43). Ertl et al. studied the effects of metallic K adsorbed on the Fe(100) face on the synthesis of ammonia (VII-43). It was found that the work function decreased with increasing K coverage with a minimum value of $\Delta_{\phi}=-2.35$ eV at 4 x 10^{14}K atoms/cm^2 and that the initial dipole moment of the K-iron complex was 4.4 debye indicating that essentially all of the valence electrons of K had been transferred to the iron surface. At a concentration of 1.5 x 10^{14} K atoms/cm^2 it was found that the rate of N_2 dissociation was increased by a factor of 300 as compared to a clean Fe(100) surface. In addition it was found that K eliminates the activation energy of N_2 dissociative adsorption and that the heat of adsorption of molecular N_2 increased by 11.5 kcal/mol (Figure VII-8). The heat of adsorption was 3 kcal/mol