more than that on a clean Fe(100) surface. From the potential energy diagram shown in Figure VII-8, it is seen that K decreases the potential minimum of molecular N_2 adsorption which lowers the activation energy of N_2 dissociation (point B).

It has been proposed by Ertl that the effect of K promotion on N_2 chemisorption is electronic in nature (VII-9). The decrease in the work function when iron is promoted with K indicates that the energy level between the highest occupied d-state and the lowest unoccupied d-state is decreased. In addition, the increase in electronic density on the Fe surface near a K atom increases the strength of back donation of Fe d-electrons into the N_2 π_g^* orbital which increases the M-N_2 bond strength and decreases the N-N bond strength. This is analogous to the mechanism of K promotion proposed by Dry et al. for the dissociation of CO on transition metals (VII-31).

CO and H_2 Co-Adsorption

Several studies of the coadsorption of CO and H_2 have been done on transition metals and it has been concluded that some sort of a surface complex between adsorbed hydrogen and CO forms. Benzinger and Madix, studying the coadsorption of CO and H_2 on Fe(100), have presented some evidence that the surface complex may be adsorbed methyl groups (VII-44). TPD experiments in which a Fe(100) surface was first exposed to CO and then H_2 were performed. Increasing the CO pre-coverage produced a lowering of the H_2 sticking probability such that after a 4 L exposure to CO, no hydrogen adsorption was detected. The CO desorption spectra for these experiments were identical to those obtained when only CO was adsorbed: however, the H_2 desorption spectra shifted to higher temperature and became weaker

with increasing CO coverages. It was concluded that preadsorbed CO physically blocked the adsorption of H_2; however, the binding energies of CO and H_2 were not altered.

The preadsorption of H_2 followed by the adsorption of CO gave quite different TPD results. It was found that increasing the amount of CO exposure did not produce an increase in the amount of H_2 desorbed. Desorption of H_2 when the Fe(100) surface was treated with only H_2 occurred at about 400 K. However, when CO was exposed to the H_2 pre-exposed surface, this peak moved to lower temperatures and a new peak at 475 K appeared. In addition this new peak increased in intensity with increasing coverages of hydrogen. CO desorption experiments showed that the amount of CO desorbing above 400 K was reduced by preadsorbed H_2. Most significantly, the amount of CO desorbing which corresponds to dissociated CO decreased greatly.

The two H_2 desorption peaks when H_2 is preadsorbed followed by CO exposure indicated that hydrogen interacts in two ways: (1) remains bound to the iron surface as H atoms or (2) interacts with adsorbed CO to produce an intermediate. Since the H_2 desorption peak at 400 K, corresponding to adsorbed atomic H, moves to lower temperature with increasing exposure to CO, it was concluded that CO weakens the binding energy of hydrogen. No CO desorption peak was observed at 475 K for this set of experiments, so the intermediate formed by H_2 adsorption followed by CO adsorption did not decompose to CO. Benzinger and Madix concluded that the 475 K H_2 desorption peak was the result of hydrogen interacting with CO prior to dissociation or the result of the decomposition of methyl groups to H_2 and surface carbon. It was found that the adsorption of methyl chloride

to give adsorbed methyl groups gave a H_2 TPD peak at 475 K. This similarity led them to conclude that methyl groups were responsible for the 475 K peak seen in the H_2 desorption experiments.

Coadsorption studies performed by Wedler et al. (VII-45) are consistent with those of Benzinger and Madix (VII-44). Preadsorption of CO with coverages $\theta_{total} \leq 0.53$ followed by adsorption with H_2 produces a hydrogen β_2 state. When more H_2 is added giving $\theta_{total} > 0.55$ a transformation corresponding to $\beta_2 \rightarrow \beta_1$ occurs. This same transformation occurs when only H_2 is adsorbed at $\theta \sim 0.5$. Since this $\beta_2 \rightarrow \beta_1$ transformation occurs even when CO is preadsorbed, it was concluded that some sort of interaction between hydrogen and CO occurred. This was demonstrated by an increase in the heat of adsorption of hydrogen for increasing CO preadsorption coverages. It was concluded that what ever the interaction is, it occurs through "bonding electrons of the iron surface, rather than a direct route leading to surface complex formation." In the converse case, when H_2 was preadsorbed and the iron was then exposed to CO, hydrogen was eventually displaced by high coverages of CO. It was concluded that CO interacts with hydrogen (as mentioned above) to produce a transformation from strongly bound β_2 hydrogen to weakly bound β_1 hydrogen which is capable of desorbing at 270K. Despite concluding that an interaction between hydrogen and CO takes place, no reaction intermediates were identified or proposed.

Dittrich et al. have also studied the coadsorption of CO and H_2 on Fe, Co, Ni and FeCo films and have obtained similar results as shown above (VII-46). In particular, it was found that preadsorbed CO decreases the ability of hydrogen to

chemisorb and that CO can partially displace preadsorbed hydrogen. Simultaneous adsorption of CO and hydrogen revealed that the amount of CO adsorbed is only slightly less than if CO alone had been adsorbed while the amount of hydrogen adsorbed was half that if hydrogen alone had been adsorbed. Adsorption of a mixture of ^{13}CO and $C^{18}O$ followed by desorption showed that no isotopic mixing occurred upon desorption *i.e.,* no $^{13}C^{18}O$ or CO were detected in the desorbed gas. However, when a mixture of H_2 and D_2 were adsorbed followed by desorption, complete isotopic mixing occurred *i.e.*, HD was detected. These results indicate that desorption of CO and H_2 are first and second order processes respectively. During their coadsorption experiments no reaction products were detected. This led them to determine the minimum pressure required for the hydrogenation of surface carbon, the proposed first step of the FT synthesis. They considered a surface lattice with four nearest neighbors in their model. The surface carbon present had a coverage $\theta_c=1/Z=1/4$ and the coverage of hydrogen was $2/Z=1/2$. It was determined that if CH_2 formation is the rate limiting step, then the rate of product formation is proportional to $\theta_c(\theta_H)^2$; therefore, in order for hydrogenation to take place, the value of $\theta_c(\theta_H)^2$ should be greater than $1/Z(2/Z)^2$. Values of $\theta_c(\theta_H)^2$ were derived from a series of "coupled differential equations" derived in their work. Plotting these values versus pressure revealed that at $\theta_c(\theta_H)^2 = 1/Z(2/Z)^2 = 1/16$, the pressure is about 10 Pa between 500 and 650K.

Kinetic studies of the methanation reaction have indicated that the dissociation of CO on catalyst surfaces is hydrogen assisted. Assuming that a surface carbon species is an intermediate in methanation, the results of Ho and Harriot with Ni/SiO_2 catalysts indicate that simple dissociation of CO and reactions of surface carbon with

hydrogen do not control the kinetics of the reaction (VII-47). Instead they proposed the following reaction steps:

$$CO_{(g)} + S \leftrightarrow CO_{ads} \quad \text{(i)}$$

$$H_{2(g)} + S \leftrightarrow 2H_{ads} \quad \text{(ii)}$$

$$CO_{ads} + 2H_{ads} \rightarrow C_{ads} + H_2O \quad \text{(iii)}$$

$$C_{ads} + 4H_{ads} \rightarrow CH_4 \quad \text{(iv)}$$

For the rate determining step (iii), they assumed 2 H atoms react in order to account for a reaction order of hydrogen up to 1; however, they claimed that reaction (iii) can also be explained as

$$CO_{ads} + H_{ads} \leftrightarrow COH_{ads} \quad \text{(v)}$$

$$COH_{ads} + H_{ads} \xrightarrow{\text{slow}} C_{ads} + H_2O \quad \text{(vi)}$$

Similar conclusions were reached by Wang et al. in kinetic studies of methanation using supported Pd catalysts (VII-48). They proposed the following reaction steps for the dissociation of CO:

$$CO \leftrightarrow CO_{ads} \quad \text{(vii)}$$

$$H_2 \leftrightarrow 2H_{ads} \quad \text{(viii)}$$

$$CO_{ads} + yH_{ads} \rightarrow C_{ads} + H_yO_{ads} \quad \text{(ix)}$$

$$H_yO_{ads} + H_{ads} \rightarrow H_2O \quad \text{(x)}$$

$$C_{ads} + 4H_{ads} \rightarrow CH_4 \quad \text{(xi)}$$

where step ix is rate determining.

Blyholder and Lawless have studied the hydrogen assisted dissociation of CO on the (100) face of a Fe_{12} cluster using molecular orbital calculations (VII-49). It was found that unassisted dissociation of CO with the lowest activation energy would

occur over the center of a four-fold site. The effect of a hydrogen atom on dissociation of CO at this site was examined with the hydrogen atom interacting with the carbon atom or oxygen atom of CO. The activation energy of CO dissociation when hydrogen interacts with the carbon is 22 kcal/mol less than when hydrogen interacts with the oxygen atom. Interestingly, it was found that the interaction of hydrogen with the oxygen of CO did not lower the activation energy significantly. The structure of the HCO intermediate is shown in Figure VII-9. The C-O bond length has expanded from 1.128 Å for free CO to 2.2 Å thus indicating a substantial weakening of the C-O bond.

Bianchi and Bennet have studied the hydrogen assisted dissociation of CO on a reduced 10%Fe/Al_2O_3 catalyst (VII-50). They measured the extent of CO dissociation in terms of the rate of carbon deposition when either a 10% CO/1%H_2/89%He mixture or 10% CO/90% He mixture was passed over the catalyst at 270°C. The rate of carbon deposition was determined according to the amount of CO_2 liberated since, according to the reactions,

$$CO_{(g)} \rightarrow CO_{ads} \qquad \text{(xii)}$$

$$CO_{ads} \rightarrow C_{ads} + O_{ads} \qquad \text{(xiii)}$$

$$O_{ads} + CO_{(g)} \text{ or } CO_{ads} \rightarrow CO_{2(g)} \qquad \text{(xiv)}$$

for every molecule of CO_2 produced, one C atom is deposited on the surface of the catalyst. A direct determination of carbon deposition was also obtained by hydrogenation of the catalyst after carburization. The amount of CH_4 produced essentially indicated the amount of carbon deposited. For the 10% CO/1% H_2/89% He run, the ratio of CH_4/CO_2 was 2.25 at the beginning of the run but decreased to

slightly below 1 at the end of the run. In the case of the run made with 10% CO/90% He, the CH_4/CO_2 ratio remained approximately 1 throughout the run indicating that all of the oxygen was removed as CO_2. The CH_4/CO_2 ratio being greater than 1 for the 10% CO/1% H_2/89% He run means that the adsorbed oxygen on the surface of the catalyst is not removed by CO in the form of CO_2. Since no H_2O was detected during the run, it was concluded that hydrogen must stabilize some oxygen species on the surface of the catalyst. In addition it was found that the extent of carbon deposition, as determined by hydrogenation of the catalyst was much greater for the run using 1% H_2. These results seem to indicate that H_2 assists in the dissociation of CO. Since no water was detected during the 1% H_2 run, these results contradict Ho and Harriot (VII-47) as seen in reaction iii. Bianchi and Bennet claim that the hydrogen assisted dissociation proposed by Wang et al. (VII-48) may be consistent with their finding when y, from reaction ix, is equal to 1. In this case, adsorbed OH would be formed and the hydrogen assisted steps would be:

$$H_{2(g)} \leftrightarrow 2H_{ads} \qquad \text{(xv)}$$

$$CO_{ads} + H_{ads} \rightarrow C_{ads} + OH_{ads} \qquad \text{(xvi)}$$

In Bianchi and Bennet's work, the 1% H_2 feed was low enough to keep y=1; however, in the case of the FT synthesis where H_2 is about 40-60%, y=2 and H_2O is formed. The decrease of the CH_4/CO_2 ratio to 1 towards the end of the run indicates that the OH species formed during the beginning of the run is converted to CO_2 according to:

$$OH_{ads} + CO_{ads} \text{ or } CO_{(g)} \rightarrow CO_2 + H_2. \qquad \text{(xvii)}$$

Since the OH species is lost after some time on stream, it was proposed that this occurs during the bulk carbidization of the catalyst, i.e., conversion of the metallic catalyst to carbide weakens the M-OH bond.

Intermediate Species Produced after CO and H_2 Dissociation

Erley et al., studying the FTS over a Fe(110) single crystal were able to identify adsorbed CH_x intermediates on the surface of the crystal (VII-51). Following FTS and evacuation of the reactor, EELS revealed intense loss peaks at 3100, 3010 and 1420 cm^{-1}. The loss peaks at 3010 and 1420 cm^{-1} matched quite well with those obtained on a Fe(110) face by the decomposition of acetylene with peaks at 3050 (C-H stretching) and 880 cm^{-1} (C-H bend). A loss peak was also observed at 1190 cm^{-1} which is characteristic of C-C bonds. It was also concluded that the peak at 3100 cm^{-1} was partially related to the peak at 1190 cm^{-1} based on the same dependence of the intensity of these peaks with different CO/H_2 ratios. CH_2 groups bound to surface carbon give similar EELS so it was concluded that these peaks are from a bound M-$C{=}CH_2$ species. EELS of a carbon covered Fe(110) surface which was exposed to hydrogen were identical to those of the FT run. If it is assumed that the species identified in this study are intermediates in the FTS, then the hydrogenation of molecularly adsorbed CO is not necessary as an intermediate for C-H bond formation and C-C bond formation.

Some investigators have utilized extended Huckel calculations to determine the nature of the chemisorption of CH_x groups on transition metals (VII-52,VII-53). Zheng et al., studying Ti(0001), Cr(110) and Co(0001) came to the conclusion that CH_x species bond to the metal surface in such a way as to replace the missing H

atoms with metal atoms (VII-52). Methyl groups tend to bond on top, CH_2 species bond in a two-fold bridging mode and CH species bond in a three-fold capping mode. De Koster and Santen came to similar conclusions with Rh(111) and Ni(111) surfaces (VII-53). In addition, it was found that CH_2 will bind in one fold sites at high Fermi level and CH_3 will bind at two-fold sites for lower Fermi level. Interestingly, Zhang et al. also determined that the mobility of CH_x fragments decreases and the coupling energies of CH_x fragments increases upon moving left to right across the periodic table. These two affects oppose each other presumably resulting in a maximum of FT activity in the middle of the transition metal series (Fe, Co, Ru etc.) (VII-52).

The incorporation of surface carbon into CH_4 and higher carbon number products during methanation and FTS has been studied by Biloen et al. using isotope tracers (VII-54). In their experiments, a known amount of ^{13}C was adsorbed onto the surface of either a Ni, Co or Ru catalyst by the disproportionation of ^{13}CO; $^{12}CO/H_2$ was then passed over the catalyst under synthesis conditions.

According to Biloen et al., the time needed to convert a reactant CO molecule into products is given by the total time τ (VII-54). The rate of product formation in their study is then given as

$$\frac{dN_p}{dt} = \left(\frac{1}{\tau}\right) \sum_i n_i \qquad \text{[VII-14]}$$

where $\sum_i N_i$ is the total number of chemisorbed intermediates in the steady state. In terms of a reaction intermediate, C_i, the time needed to convert C_i into products must be less than or equal to the total time needed to convert a CO molecule into products.

$$\tau_I \leq \tau \qquad \text{[VII-15]}$$

In the case of this experiment, the reaction intermediate was labeled ^{13}C deposited on the catalyst. The rate of labeled product formation was given as

$$\frac{dN_p}{dt} = \left(\frac{1}{\tau_I}\right) N_I \qquad \text{[VII-16]}$$

The synthesis part of the experiment was run until 20% of the ^{13}C on the surface of the catalyst had been reacted and then stopped. The isotopic distributions of the products were determined and then the synthesis was run again until another 20% of the ^{13}C had been consumed. This process was repeated several times for the different catalysts.

In the case of the Ni catalyst, the percentage of $^{13}CH_4$ in the total CH_4 produced was found to increase with an increase in the surface coverage of ^{13}C, as expected. Isotopic examination of the higher carbon number products surprisingly revealed that several ^{13}C atoms were incorporated into the same molecules. In the case of propane, 17% of the initially formed molecules were $^{13}C_3H_8$ and 37% contained 2 ^{13}C atoms. Butane also had significant amounts of multiple ^{13}C atoms present per molecule; however, no $^{13}C_4H_{10}$ was identified. It was found that the tendency to incorporate ^{13}C into the skeletons of the hydrocarbons decreased as the surface coverage of the ^{13}C decreased. It is interesting to note that the percentage of ^{13}C incorporated into the different carbon number products was equivalent. Experimental results showed that $\tau 12_{CO}$ and $\tau 13_{CO}$ are equal. Going back to reaction iii, this indicates that CO dissociation is not the rate determining step of methanation. It also indicates, according to the authors, that a carbide species, CH_x, is the most abundant

active species, not adsorbed CO. Since the ^{13}C content of methane and the higher carbon number products were equal, it was determined that the FTS and methanation proceed through a common intermediate. Although they claim molecularly adsorbed CO may be involved in the synthesis of oxygenated products, the main reaction pathway to hydrocarbons by methanation and the FTS was proposed to be $C_mH_y + CH_x \rightarrow C_{m+1}H_{x+y}$, where x=0-3 but probably with x=2 and y=2m+1 (VII-54).

Baetzold has presented work aimed at the determination of the heats of reaction of CH_x intermediates in the synthesis of methane and hydrocarbons over transition metal catalysts (VII-55). In the first step, the enthalpy changes for the following reactions were calculated:

$$C_{ads} + H_{ads} \rightarrow CH_{ads} \qquad \Delta H_1 = -4 \text{ to } -2 \text{ kcal/mol} \qquad \text{(xviii)}$$

$$CH_{ads} + H_{ads} \rightarrow CH_{2,ads} \qquad \Delta H_1 = 11 \text{ to } 16 \text{ kcal/mol} \qquad \text{(xix)}$$

$$CH_{2,ads} + H_{ads} \rightarrow CH_{3,ads} \qquad \Delta H_1 = -6 \text{ to } 0 \text{ kcal/mol} \qquad \text{(xx)}$$

$$CH_{3,ads} + H_{ads} \rightarrow CH_{4,ads} \qquad \Delta H_1 = 17 \text{ to } 22 \text{ kcal/mol} \qquad \text{(xxi)}$$

Based on experimental values of C-H bond energy, heat of C adsorption, heat of hydrogen adsorption and calculated values of CH_x adsorption,

$$\Delta H = \text{B.E.} + Q_{CH} - Q_H - Q_C. \qquad \text{[VII-17]}$$

These values were calculated and compared for ending transition metals (Ni column) and middle transition metals (Fe column). In general the heats of reaction are greater for the ending transition metals than they are for the late transition metals, indicating that they are better hydrogenation catalysts (VII-55).

Rate constants for the above reactions were calculated by the equation,

$$k = k_0 e^{(-\Delta E/RT)} \qquad \text{[VII-18]}$$

where k_0 was determined from transition-state theory. The activation energy, ΔE, was calculated from the equation,

$$\Delta E_i = \Delta H_i + x, \qquad \text{[VII-19]}$$

in which "values of ΔE_i are related by the same linear constant to the enthalpy values ΔH_i." (VII-55).

In his analysis, Baetzold assumed that CO dissociates before carbon is hydrogenated. It was found that if CO and H_2 compete for the same adsorption sites on the catalyst, then the methanation rate laws showed too much of an inverse dependence on the CO partial pressure; however, CO and H_2 adsorption on distinct sites fit the rate laws. The activation energies were determined by adding a linear constant , x, from equation 19 to the value of ΔH such that the methanation turnover number was equal to experimental values. For the ending-transition metals, this value was 4 kcal and for the middle-transition metals this value was 2 kcal. The activation energy for methanation was subsequently calculated to be 27.5 kcal/mol and 23.1 kcal/mol for middle- and late-transition metals, respectively. The experimental activation energies of CO dissociation are less than the calculated activation energies of carbon hydrogenation so it was concluded that CO decomposes more easily than carbon is hydrogenated. This is in keeping with the conclusions reached by Biloen et al. that CO dissociation is not the rate determining step of methanation or the FTS (VII-54). In addition, it was found that an increase in the rate of CO dissociation produces an increase in adsorbed carbon and a decrease in adsorbed H and CH_x.

Baetzold found that the activation energies of CO dissociation were lowest for catalysts which produce long chain hydrocarbons (VII-55). This was related to the

fact that CO dissociation occurs more readily on middle-transition metals than on ending-transition metals and that high carbon number hydrocarbons are produced on the middle-transition metals. The surface concentration of CH_x (x=0 to 3), CO, and H were calculated and it was found that CH is the most abundant species ($CH>>CH_2>CH_3$). In addition, it was found that the rate limiting step of methanation is the hydrogenation of CH_3 species since the activation energy of this reaction is the highest of all the reaction steps considered.

Most studies have indicated that hydrogen adsorbed on the surface of transition metals is responsible for the hydrogenation of surface carbon and adsorbed CH_x species (VII-5 - VII-7); however, recent studies of Fe and Ni catalysts indicate bulk hydrogen is responsible for the hydrogenation activity (VII-1,VII-56). Watanabe and Wissman claim that hydrogen adsorbs as H^+, H^- , H_2- and H_2 on Fe at 23°C; however, at temperatures above 400°C no surface hydrogen could be detected (VII-1). It was concluded that the hydrogen is dissolved in the iron and that the subsurface hydrogen exists in a strain and defective layer. It was further concluded from hydrogenation of surface carbon, that the initial step is the formation of CH units by the interaction of subsurface hydrogen with the surface carbon. In other words, the carbon is hydrogenated from the "metal side." According to Johnson et al., past studies have indicated that the hydrogen content of Raney Ni catalysts influences the hydrogenation activity of catalysts; nevertheless, there was no way of telling if the hydrogen acted as an electronic modifier or as a reactant (VII-56). They developed a method of synthesizing Ni catalysts containing bulk hydrogen under low pressures ($<10^{-4}$ torr) (VII-57). In the past high pressures of hydrogen were needed to diffuse

the hydrogen into the catalyst which eliminated the ability to study the chemistry of the hydrogen at the molecular level. They have recently studied the interaction of adsorbed CH_3 species on such a catalyst which contained bulk deuterium. All D atoms adsorbed on the surface of the Ni catalyst were removed by bombardment with Xe atoms causing the surface D to desorb as D_2. Methane was then dissociatively chemisorbed on the surface of the catalyst at 80K giving adsorbed CH_3 and H. The catalyst was then heated at a rate of 2K s^{-1}. The products were monitored by mass spectrometry. When the temperature reached 180K, a rapid desorption of CH_3D occurred. This happens to be the temperature where bulk D diffuses onto the surface of the catalyst and desorbs. In another experiment, CH_4 was dissociatively adsorbed onto a clean Ni catalyst producing CH_3 and H species. Approximately 0.85 ML of H or D was then adsorbed and the temperature was increased. No CH_4 or CH_3D was observed. The only products observed were H_2 and D_2 which were produced from the adsorbed H and D and decomposed CH_3 species.

It was concluded that methane was only produced by reaction of adsorbed CH_3 with bulk deuterium. The reaction between the adsorbed CH_3 and bulk D atom was speculated to occur because the D atom lies in an interstitial octahedral site directly below the C_{3V} hollow site of the adsorbed CH_3. This puts the deuterium in good position as it diffuses to the surface because of the sp^3 configuration of CH_4. Reaction of a surface D with adsorbed CH_3 would be sterically hindered. This has great relevance in terms of hydrogenation on other metals, in particular the FTS synthesis on Fe, Co and Ru. Since the hybridization of an adsorbed RCH_2 species is nearly identical to adsorbed CH_3, it is possible that one of the termination steps of the FTS, namely

$$RCH_2\text{-}M + H_{bulk} \rightarrow RCH_3, \qquad \text{(xxii)}$$

proceeds by reaction with bulk hydrogen and not surface hydrogen.

Evidence for the possibility of CH_2 being the monomer in the polymerization of the FTS has been found by Brady and Pettit. They have studied the reactivity of CH_2 molecules, produced by the decomposition of CH_2N_2 on the surface of catalysts, in the absence and presence of hydrogen (VII-58,VII-59).

For the metals Ni, Pd, Fe, Co, Ru and Cu, reaction of decomposed CH_2N_2 produced only C_2H_4 and N_2 under all reaction conditions (VII-58). When H_2 gas was mixed with CH_2N_2 higher molecular weight hydrocarbons were produced. In the case of Co, Fe and Ru, C_{18} and higher hydrocarbons were produced. Polyethylene was actually produced over a hydrogen reduced Ru catalyst (VII-58). The chain length of the product and the olefin content of the catalyst decreased with higher H_2 pressure. The product distribution of a Co catalyst reacted with CH_2N_2/H_2 and CO/H_2 at 210°C and 1 atm were essentially identical. Ni and Pd catalysts also produced methane and higher molecular weight hydrocarbons; however, the same catalyst under the same conditions produced mainly methane in the presence of CO/H_2. By increasing the pressure to 68 atm, a product distribution similar to that found for the reaction of CH_2N_2 over Ni and Pd was obtained.

Brady and Pettit reasoned that the close similarity between the reactions of CH_2N_2/H_2 and CO/H_2 suggested a common intermediate (VII-58). Since CH_2N_2 decomposes over transition metals to give adsorbed CH_2 groups, the reactions are believed to proceed by the polymerization of CH_2 monomers. Since CH_2N_2 alone only gives C_2H_4, it is believed that adsorbed hydrogen plays a role in the initiation of the

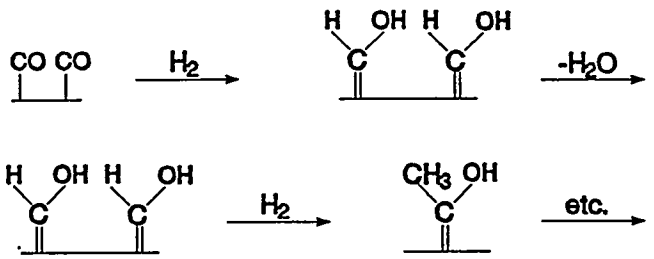
polymerization. This is supported by reactions conducted over a Cu catalyst. The reaction of CH_2N_2/H_2 over Cu catalysts only produced C_2H_4 as was the case when only CH_2N_2 was used. This was explained as a consequence of the inability of Cu to dissociatively adsorb H_2 (VII-60). Since no hydrogen was adsorbed on the catalyst, the initiation step of the polymerization could not take place. A reaction scheme proposed by Biloen et al. was suggested (VII-54). In the first step, an adsorbed CH_2 group is hydrogenated to an adsorbed CH_3 group. This step initiates successive insertions of CH_2 groups:

$$CH_{2,ads} + H_{ads} \rightarrow CH_{3,ads} \qquad \text{(xxiii)}$$

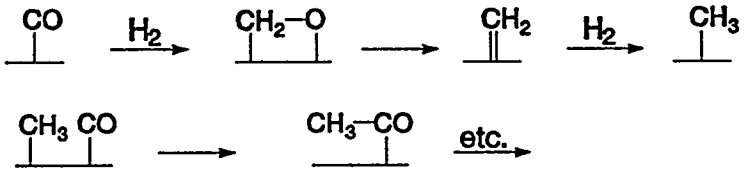
$$CH_{3,ads} + CH_{2,ads} \rightarrow CH_3CH_{2,ads} \text{ etc.} \qquad \text{(xxiv)}$$

Alkenes would result if the termination step was a β hydride elimination or an alkane would be produced if the adsorbed alkyl group was hydrogenated. It is interesting to note that de Koster and van Santen, using extended Huckel calculations, found that the coupling of CH_3 and CH_2 species does not occur due to steric interactions of the hydrogen atoms (VII-53). However, it should be pointed out that they did not consider bending of the C-H bonds to lessen the steric interactions.

This reaction mechanism, formally referred to as the Fischer-Tropsch mechanism (VII-61) was compared to the other leading reaction mechanisms proposed by Anderson (VII-62) and Emmett (VII-63) and Pichler and Shultz (VII-64,VII-59). In the Anderson and Emmett model, two adjacent molecularly adsorbed CO molecules are hydrogenated to give an enolic intermediate. Polymerization of these enolic species proceeds by condensation:



In the case of the Pichler and Shultz model, CO is adsorbed, dissociates and the carbon is hydrogenated in subsequent steps to give an adsorbed methyl group. Chain propagation then proceeds by CO insertion which has been identified in homogenous catalysis.



Since the role of CH_2 groups play different roles in these mechanisms, in the Fischer-Tropsch scheme they are involved in initiation and propagation, in the Anderson-Emmett scheme they are not involved at all and in the Pichler-Schultz scheme they are involved only in initiation, the addition of CH_2N_2 to the CO/H_2 feed stock of a FT reactor should give some indication as to which if any of these mechanisms is correct (VII-59). Brady and Pettit found that the addition of CH_2N_2 to the synthesis gas of a Co catalyzed FT reaction caused an increase in the amount of higher carbon number hydrocarbons (α increased from 0.23 to 0.51) (VII-59). Since the mechanism of Pichler and Shultz has methylene groups involved only in initiation, the addition of CH_2N_2 should only produce more product; however, the product distribution should

not change *i.e.*, α should not change. According to Brady and Pettit, the Anderson-Emmett model might produce a "bimodal distribution of products" with some product being formed by the enolic intermediate and some through the interaction of CH_2 and H_2 (VII-59). However, since only one α value was obtained from the product distribution, this is unlikely. The best explanation, in terms of these mechanisms, for the change in product distribution is that the Fischer-Tropsch scheme is operating. The increase in concentration of adsorbed CH_2 groups on the catalyst provided by CH_2N_2 would increase the likelihood of chain propagation, thereby giving a heavier product.

Brady and Pettit also use ^{13}C tracers to determine which mechanism governs the FT reaction (VII-59). In this part of the study $^{13}CO/H_2$ and $^{12}CH_2N_2$ were fed into the reactor containing a Co catalyst. Since the Anderson-Emmett model utilizes only adsorbed CO for initiation and propagation, only a product containing ^{13}C atoms should be produced. The Pichler-Shultz mechanism utilizes adsorbed CH_3 groups as initiators and adsorbed CO as a propagator. The product distribution in this case should be either ^{12}C-^{13}C-^{13}C.... or ^{13}C-^{13}C-^{13}C.... In the case of the all ^{13}C product, the CH_3 group that initiated the chain would have been synthesized by the hydrogenation of adsorbed ^{13}CO. For the case of the Fischer-Tropsch scheme, all distributions of ^{12}C and ^{13}C would be possible. By studying the ^{13}C and ^{12}C content of the propane fraction of the product, Brady and Pettit concluded that only the Fischer-Tropsch mechanism could be possible for the primary mechanism of the FTS. However, this mechanism does not explain the presence of oxygenated compounds which are known to be primary products of the FTS, so it is possible that either the Anderson-

Emmett or the Pichler-Schultz mechanisms could be responsible for the production of alcohols and aldehydes/ketones.

Similar results have been obtained by van Barneveld and Ponec by adding CH_XCl_{4-X} (X=1 to 3) to FT synthesis gas (VII-65). In contrast, Blyholder and Emmett, using ^{14}C labeled ketene, came to a different conclusion about the role of CH_X species (VII-66,VII-67). They found that ketene, when labeled in the methylene group gave a product with a constant radioactivity per mole for all carbon numbers. When ketene was labeled at the carbonyl carbon, the product had a radioactivity proportional to the carbon number. They assumed that ketene dissociated on the catalyst into adsorbed CH_2 and adsorbed CO. With this assumption, they concluded that CH_2 groups initiate chain growth but do not take place in propagation; however, adsorbed CO is responsible for chain growth. Bell has rationalized Blyholder and Emmett's results differently (VII-68). He has proposed that ketene dissociates in the presence of hydrogen to produce adsorbed CH_3 and adsorbed CO. The CH_3 group acts only as an initiator and the adsorbed CO molecule would be dissociated and hydrogenated to produce CH_X which would propagate chain growth. If correct this would explain Blyholder and Emmett's results (VII-66,VII-67) in terms of Brady and Pettit's work (VII-58,VII-59).

Shulz et al. have shown that the Anderson-Shulz-Flory plot for the sum of aldehydes and alcohols is parallel to that of linear alkanes *i.e.,* they have the same α value (VII-69). This seems to indicate that they are formed by a common intermediate. Wojciechowski has proposed that since the only difference between linear alkanes, α and β olefins, aldehydes and alcohols are their terminal groups, then

the termination step of the synthesis must determine the nature of the product (VII-5). Since two α values are obtained for linear alkanes, two termination steps must occur for alkane systems. Termination of a growing alkyl chain by reaction with an adsorbed OH species would result in an alcohol while reaction with an adsorbed H or CH_3 species would give an alkane. Carboxylation of a growing alkyl chain by an adsorbed HCO species would result in an aldehyde and so on (VII-5). Similar types of termination steps have been proposed to rationalize the production of oxygenates by the CH_X insertion mechanism (VII-53,VII-68,VII-70). Ponec has proposed that oxygenates are formed by insertion of a CO molecule into a growing alkyl chain which would be hydrogenated into an alcohol, aldehyde or carboxylic acid (VII-70).

Shustorovich has used the Bond-Order conservation approach to explore the differences in the reaction of $CO+H_2$ over Ni, Pd and Pt metal catalysts (VII-4). All three types of catalysts will produce methane; however, only Pd and Pt produce oxygenates. The methanation reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{(xxv)}$$

is 27 kcal more exothermic than the methanol synthesis reaction

$$CO + 2H_2 \rightarrow CH_3OH, \qquad \text{(xxvi)}$$

so it was assumed methanol will only be produced if the hydrogenation of H_XCO (X=0 to 3) is "kinetically preferred" over the splitting of the H_XC-O bond. The activation energy of direct dissociation of CO over Ni was calculated to be 33 kcal/mol and 29 kcal/mol for the hydrogen assisted dissociation of CO. This indicates that on Ni, surface carbon forms very easily. The decomposition of the hydrogen assisted

dissociation intermediate, HCO, into C and OH is favored over its further hydrogenation by about 15 kcal/mol.

$$HCO_{ads} \rightarrow C_{ads} + OH_{ads} \qquad \Delta E^{*}=18 \text{ kcal/mol} \qquad \text{(xxvii)}$$

$$HCO_{ads} + H_{ads} \rightarrow H_2CO_{ads} \qquad \Delta E^{*}=33 \text{ kcal/mol} \qquad \text{(xxviii)}$$

It was also pointed out that even if CH_3OH were generated, it would easily decompose to $CH_{3,\,ads} + O_{ads}$ ($\Delta E^{*}=13$ kcal/mol).

In the case of Pd (and Pt), the dissociation of CO by direct and hydrogen assisted mechanisms is endothermic, $\Delta H=50$ and 51 kcal/mol respectively. In addition, the hydrogenation of CO to HCO is favored by about 5 kcal over the hydrogenation of C to CH. This implies that this step is more important for Pd and Pt than Ni. This is in keeping with experimental results of Robbins and Maruchi-Soos where isotope labeling indicated that the formation of CH_3O did not result in the rupture of the C-O bond (VII-71). Furthermore, the activation energy of hydrogenation of bound CH_3O to CH_3OH is 16 kcal/mol for Pd versus 24 kcal/mol for Ni. All of this seems to indicate that the synthesis of methanol over Pd is at the very least competitive with the formation of methane.

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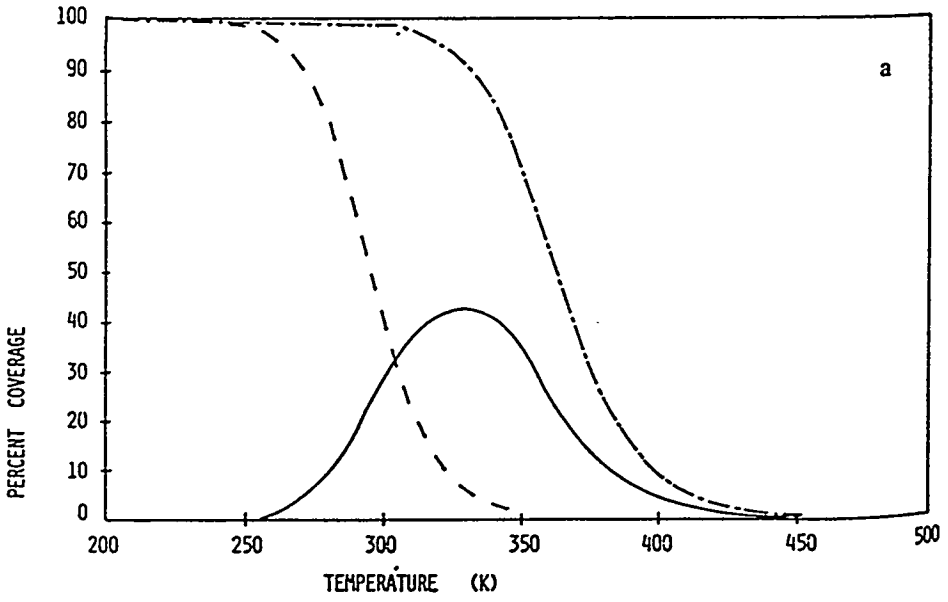
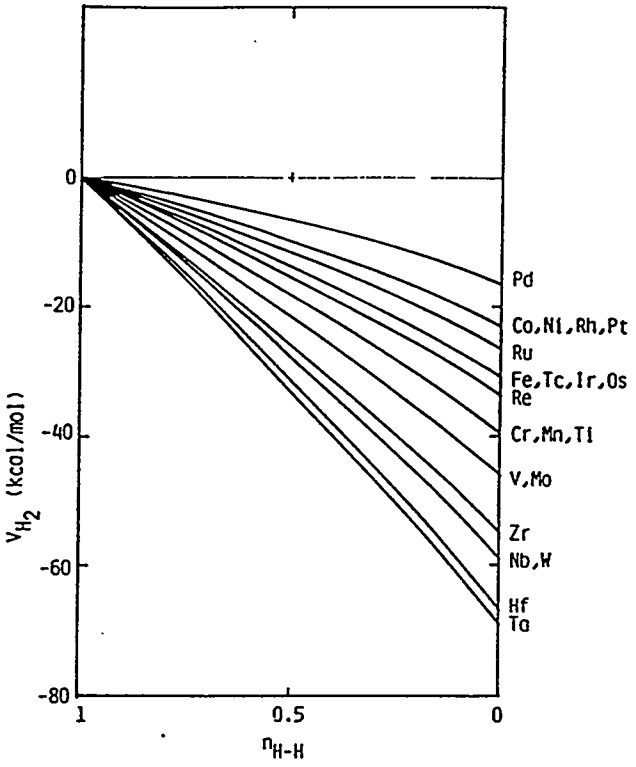
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au

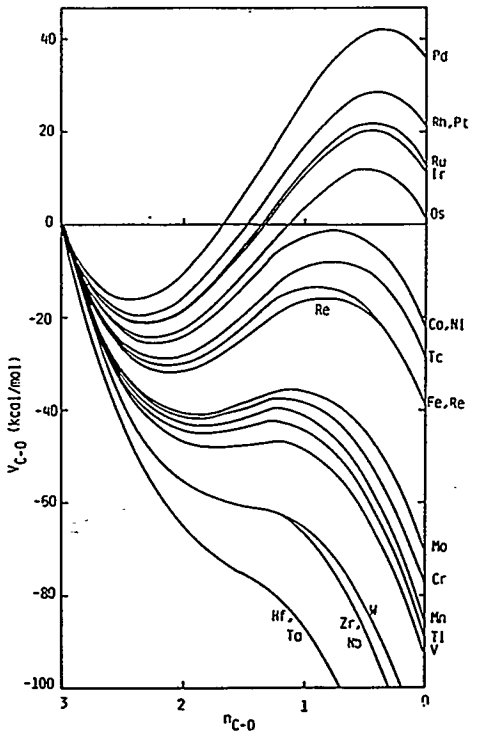
VII-1. Section of periodic table showing the border between those metals that adsorb CO dissociatively (left) and those that adsorb CO molecularly (right) (VII-18).



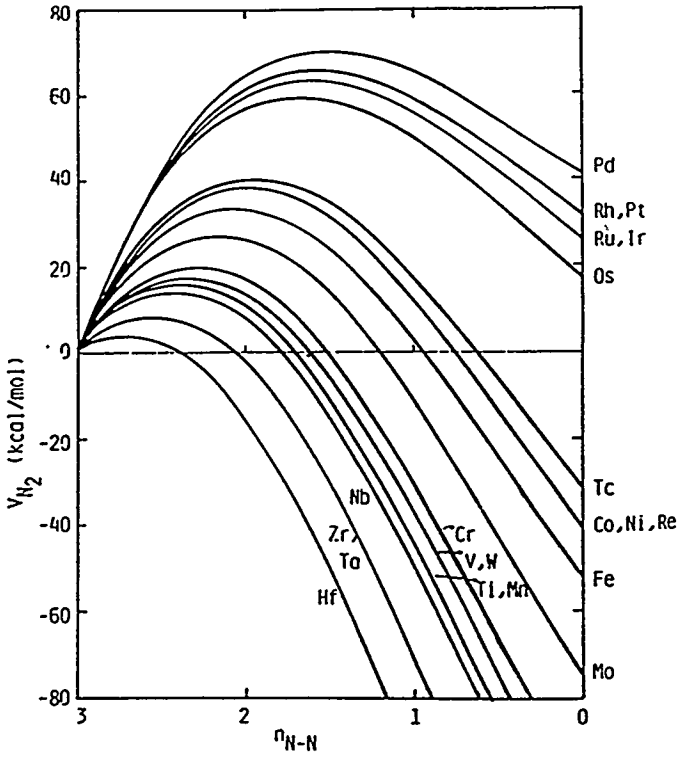
VII-2. Adsorption isobars ($P=10^{-8}$ Torr) for competitive adsorption model at ϵ_D=135 kJ/mol. -·-·- Total surface coverage. ------ molecular adsorption. —— dissociative adsorption (VII-20).



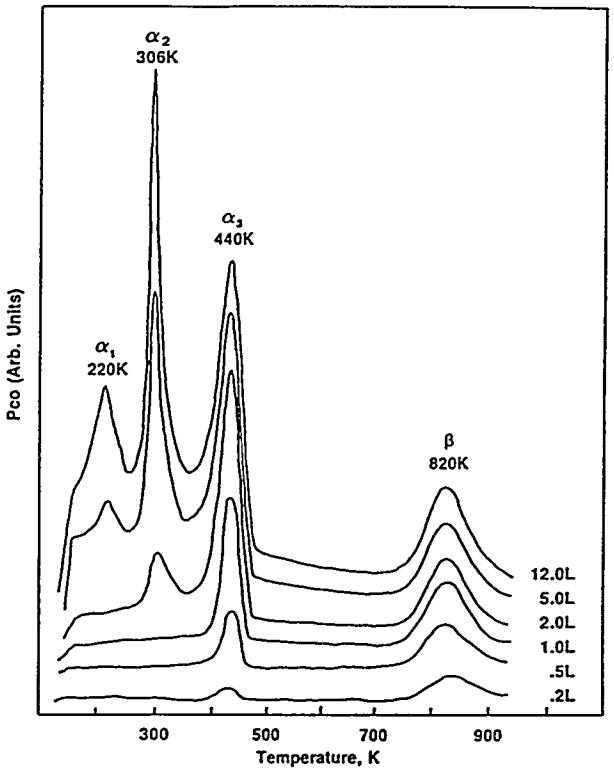
VII-3. Interaction energy between a H_2 molecule and a transition metal surface, V_{H_2} as a function of bond order, n_{H-H} (VII-8).



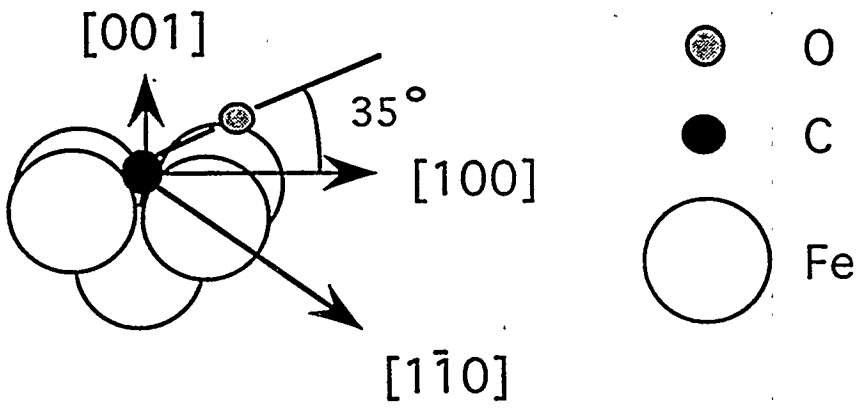
VII-4. Interaction energy between a CO molecule and a transition metal surface, V_{CO} as a function of bond order, n_{C-O} (VII-8).



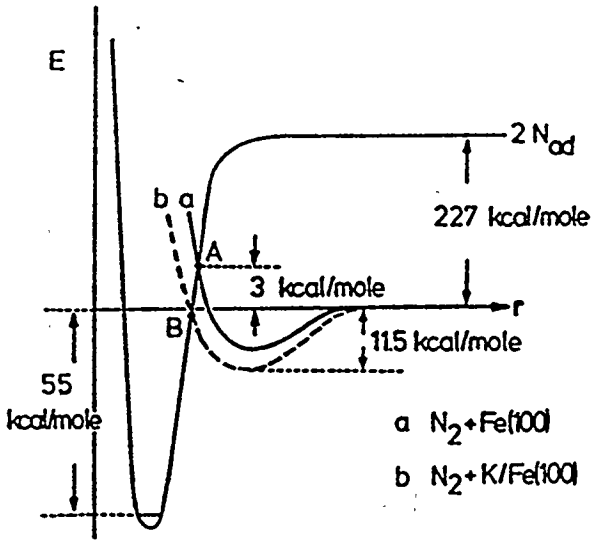
VII-5. Interaction energy between a N_2 molecule and a transition metal surface, V_{N_2} as a function of bond order, n_{N-N} (VII-8)



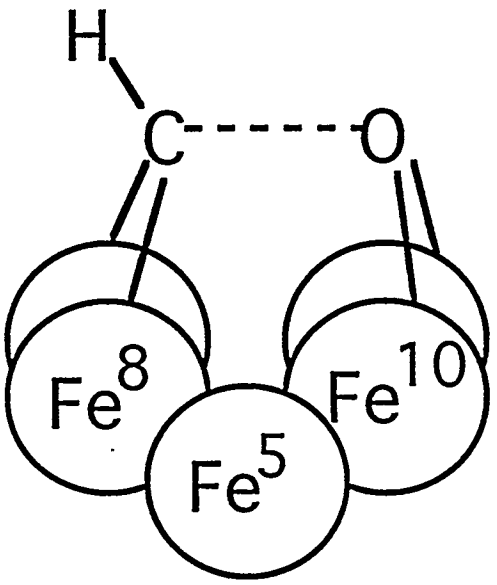
VII-6. Thermal desorption spectra as a function of CO exposure for a clean Fe(100) surface at 150 K (VII-22).



VII-7. Bonding of a CO molecule to a four fold hollow on a Fe(100) face (VII-25).



VII-8. Potential energy diagram for dissociative and molecular adsorption of N_2 on a clean and K covered Fe(100) surface (VII-43).



VII-9. Structure of activated complex for H on C assisted dissociation of CO on a Fe_{12} cluster (VII-49).