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# CO-Induced Ethane Formation from Ethylene and Hydrogen on Fe(100): Effects of Ligands in Surface Reactions

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**Abstract:** When $C_2H_4$ alone is adsorbed on a hydrogen-presaturated Fe(100) surface (Fe(100)-H) without coadsorbed CO, reversible formation of ethyl groups ($C_2H_5$) occurs, and no ethane is observed. Remarkably, the coadsorption of CO with ethylene on Fe(100)-H induces the facile formation of ethane at 170 K. The coadsorption of CO weakens Fe-H bonds and appears to induce ethane formation by reducing the activation barrier for the reductive elimination reaction between H adatoms and adsorbed ethyl groups. The observed activation barrier for this reaction is approximately 5-6 kcal/mol. When CO is adsorbed onto Fe(100)-H *before* $C_2H_4$ adsorption, the maximum ethane yield is achieved with a CO coverage of 0.2 ML. At a CO saturation coverage of 0.5 ML no ethylene will adsorb, and thus no ethane is formed. When CO is adsorbed onto Fe(100)-H *after* $C_2H_4$, the ethane yield is reduced at high CO exposures due to displacement of ethylene by CO. Similarly, high exposures of CO onto an Fe(100)-H surface covered with ethyl groups led to the displacement of ethane. Ethane formation at H precoverages below saturation requires a threshold CO coverage governed by the relationship $4\theta_{CO} + \theta_H \geq 1$. CO adsorbed at coverages below the threshold coverage appears to compress H adatoms into regions of locally higher concentration. Apparently CO must bind within surface regions locally concentrated with H in order to induce ethane formation.

## 1. Introduction

We report here the first documented case of CO-induced hydrogenation on a metal surface. We present elsewhere evidence that ethylene undergoes a migratory insertion reaction on hydrogen-presaturated Fe(100) to form stable ethyl groups.[1] In that case even though excess hydrogen is present, the ethyl groups and adsorbed hydrogen ($H_{(a)}$) do not undergo reductive elimination to form ethane, but rather the ethyl groups decompose via $\beta$-hydride elimination to liberate ethylene to the gas phase. We have extended our studies of the reactions of ethylene on H-covered Fe(100) to include coadsorbed CO. The motivating factor was the reactivity displayed by transition metal-alkyl-carbonyl complexes, in which CO often undergoes migratory insertion into the M-alkyl bond to form an acyl.[2] In the process of studying such reactions we discovered that coadsorbed CO promotes the reductive elimination of ethane with high selectivity. The origin of this effect appears to be the destabilization of adsorbed H atoms by CO.

White[3] and Akhter and White[4,5] have recently reviewed the effects of coadsorbed CO on reactions occurring on surfaces of single crystals of transition metals under ultrahigh vacuum (UHV). Aside from CO oxidation reactions, most of the research on CO coadsorption has focussed on systems in which adsorption and desorption are the only reactions involved. Coadsorption of CO with hydrogen has been studied quite extensively, and several generalizations have been drawn from the results.[20-25] As will be seen below, the phase behavior of coadsorbed CO and H is

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important in the hydrogenation of ethylene. The phase behavior of the CO–H adlayer depends on the structure of the surface. CO adsorbed onto a hydrogen-presaturated surface forms a mixed adlayer on open faces of transition metals; for example, on bcc (100), fcc (100), and fcc (110) surfaces[3-5] no phase separation occurs. However, on close-packed faces, i.e. fcc (111) and hcp (001), CO does not bind in the midst of H-saturated regions, and segregated structures form;[3-5] displacement of $H_2$ by CO has been documented in a few cases. Strong CO–H repulsion is responsible for the inhibition of CO adsorption in H-saturated islands on close-packed surfaces. This interaction energy is apparently reduced by the greater CO–H distances present on open surfaces, allowing CO to adsorb in H-saturated regions without displacing $H_2$. However, the repulsive interactions are still considerable on open surfaces, as evidenced by CO-induced low-temperature desorption states of $H_2$ (e.g. <200 K) on the (100) faces of Ni, Rh, and W.

Reactions other than desorption can also be greatly influenced by coadsorbed CO, as indicated by changes in the kinetics and selectivity of the decomposition of ethylene on Ni(100),[6] Ru(001),[7,8] and Rh(100).[9] On the CO-free Ru(001) surface ethylene initially decomposes to form both acetylide (CCH) and ethylidyne ($CCH_3$) in competing pathways.[7,8] The same species are formed in the presence of coadsorbed CO, but the selectivity is shifted to favor acetylide. CO also alters the selectivity of ethylene decomposition on Rh(100).[9] The primary pathway on the CO-free surface is the formation of acetylide, with ethylidyne produced only for ethylene coverages over 0.5 ML.[10] On a Rh(100) surface precovered with 0.5 ML of CO, however, the decomposition of $C_2H_4$ proceeds entirely via ethylidyne.

In these cases CO primarily acts as an inhibitor of surface reactions by blocking sites required for decomposition. For example, ethylene decomposition on Ni(100) is inhibited by postsaturation coverages of CO;[6] the ethylene desorbs intact rather than decomposing as it would on the CO-free surface. Postsaturation coverages of CO also stabilize hydrocarbon fragments produced from ethylene decomposition, i.e. ethylidyne on Ru(001)[7,8] and various $C_2H_x$ species, including vinyl ($CHCH_2$), on Ni(100).[6] Decomposition of these fragments normally occurs at temperatures below the CO desorption temperature. However, sites required in the decomposition are blocked until CO begins to desorb and thus the hydrocarbon species are stabilized up to that temperature. Site blockage is not responsible for the effects we report here.

Studies of the coadsorption of CO and hydrogen on Fe(100) have been reported by Benziger and Madix[11] and by ourselves.[12] The earlier results were incomplete, since hydrogen coverages only much lower than saturation were studied. The results of our studies on the adsorption of CO[12] and of $C_2H_4$[1] on hydrogen-covered Fe(100) are germane to this current study, and are summarized below in Sections 3.1 and 3.2, respectively. Briefly, CO adsorbs on the H-presaturated Fe(100) surface (designated Fe(100)–H) to induce several low-temperature $H_2$ desorption states ($\gamma$ states) without displacement of hydrogen, indicating the formation of a mixed adlayer, similar to the behavior observed for other open faces of transition metals. If CO is adsorbed prior to $H_2$, hydrogen uptake is reduced and no $\gamma$-$H_2$ states are formed. The CO-induced $\gamma$ desorption states of $H_2$ appear to arise from CO adsorbed in regions with a local H saturation coverage of 1 mL. Ethylene adsorbs molecularly on Fe(100)–H; molecular desorption competes with the reaction with H adatoms to form ethyl groups. As stated above, ethyl groups undergo $\beta$-hydride elimination to liberate gas-phase ethylene, and no ethane is formed.

## 2. Experimental Section

All experiments were performed in a stainless steel UHV chamber with a base pressure of 1 × $10^{-10}$ Torr. Temperature-programmed desorption and reaction (TPD/TPRS) experiments utilized a quadrupole mass spectrometer (UTI 100C) modified with a collimating orifice approximately 0.8 cm in diameter. A chromel–alumel thermocouple was spotwelded to the Fe(100) sample, and the mass spectrometer and thermocouple signals were interfaced to a computer. The mass spectrometer signal was multiplexed so that up to eight masses could be monitored in a single experiment. A liquid nitrogen cooling system allowed sample temperatures as low as 110 K to be reached. Two capillary array dosers were used so that contamination of a given gas sample by other gases being used was minimized. Surface elemental composition was determined by Auger electron spectroscopy (AES), and long-range ordering of adsorbates was monitored using low-energy electron diffraction (LEED).

Details of the preparation and initial cleaning of the Fe(100) crystal are given elsewhere.[12] Routine cleaning was achieved by Ar ion bombardment with a sample temperature of 700 K. This temperature was high enough to allow diffusion of impurities from the bulk but low enough so that carbon preferentially accumulated at the surface rather than in the bulk so it could be sputtered away more effectively. After each bombardment the crystal was annealed at 1020 K for 30 s. This treatment resulted in a sharp p(1×1) LEED pattern and allowed us to determine that bulk impurity levels were low enough to prevent impurity segregation to the surface at the high temperatures reached during a TPRS scan. Surface cleanliness was determined by AES with absolute coverages of carbon, oxygen, and sulfur calibrated according to known LEED patterns. Carbided and sulfided Fe(100) each display a c(2×2) pattern at the adatom saturation coverages of 0.5 ML, where 1 ML equals the Fe(100) surface atom density of 1.22 × $10^{15}$ atom/$cm^2$. A c(2×2) pattern is also formed by saturation of the CO dissociative state, resulting in surface coverages of 0.25 ML each for both carbon and oxygen. Our cleaning procedures resulted in surface carbon levels of approximately 0.03 ML, with oxygen levels of 0.01–0.02 ML.

TPD/TPRS experiments were performed by dosing gases while the Fe sample was held at its base temperature of 110 K and by desorbing species through the collimator directly into the mass spectrometer. Gases were dosed directly by placing the crystal approximately 0.5 cm in front of the doser. Details of the dosing procedures are given in the figure captions. In all cases except those described in Section 3.4 the surface was first saturated with adsorbed H atoms. Absolute exposures of hydrogen were calibrated via a combination of background and direct doses as described previously.[12] Both ethylene and CO have high sticking probabilities as well as large enhancement factors for direct dosing, the sum of which results in a large uncertainty in experimental values of the exposure. Absolute ethylene and CO exposures therefore were not determined.

Absolute coverages of ethylene evolved during TPRS were estimated by a hydrogen and deuterium balance in the H–D exchange reaction of $C_2H_4$ on D-saturated Fe(100).[1] No decomposition of ethylene occurs on this surface and the only gas-phase products evolved are hydrogen, ethylene, and their isotopes. The coverage of H adatoms deposited in this reaction thus must equal the D atom content of the desorbing ethylene. The TPRS traces of deuterated ethylenes were deconvoluted to correct for mass spectral fragmentation. By using the hydrogen saturation coverage of 1.0 ML as a calibration standard along with the hydrogen–deuterium balance, ethylene TPRS areas have been converted to surface coverages. Stated ethylene coverages are accurate to ±20%.[1] However, absolute coverages of ethane evolved during TPRS were estimated by calibrating the sensitivity of the mass spectrometer for ethane relative to ethylene. The surface coverage/TPRS area ratio for ethylene discussed above was used as a calibration standard. Mass spectral cracking patterns for ethane and ethylene were measured. Cracking patterns were corrected for ionization probabilities,[13] mass spectrometer gain, and quadrupole transmission efficiency.[14] The same mass spectrometer was used for the calibration as was used in TPD/TPRS experiments. The resulting mass spectral correction factor was 3.40 for $C_2H_6$ (*m*/*q* 30); the integrated TPRS areas of ethane were multiplied by this factor to normalize yields with respect to ethylene (*m*/*q* 28). Stated ethane yields have an estimated error range of approximately ±25% (Section 3.3.1). Absolute calibration of CO TPD areas consisted of dosing CO on Fe(100) at 425 K in order to fill the dissociated CO state. This state saturates at 0.25 ML of CO; associated recombination of carbon and oxygen occurs to regenerate gas-phase CO at 800 K. The TPD area at

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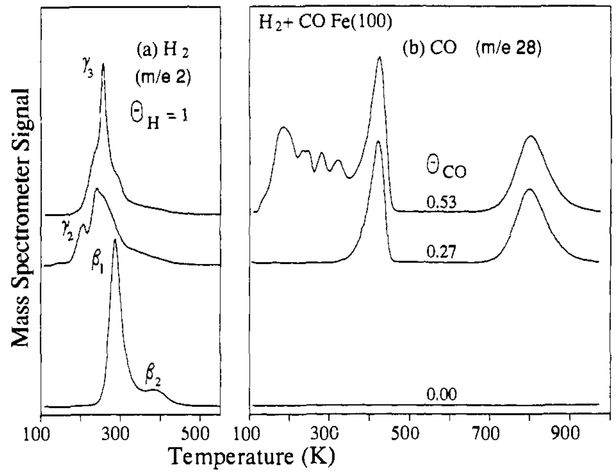

**Figure 1.** Temperature-programmed desorption of (a) $H_2$ and (b) CO for several CO exposures on H-presaturated Fe(100). Heating rates are approximately 10 deg/s.

saturation of this $\beta$ state was used as a calibration standard.

Since our collimated mass spectrometer detects products in a line-of-sight configuration directly as they desorb, and since the signals reflect gas-phase molecular densities and not fluxes (see e.g. ref 15), a $T_s^{1/2}$ correction was made for the evolution temperatures of all desorbing species. This correction is based on the assumption that the translational energy of desorbing molecules scales with the temperature of the surface during desorption and that angular profiles for desorption for all hydrocarbon states are the same as that of the ethylene standard. Hydrogen and CO coverages were determined independently, thus no assumptions have been made about the angular profiles of $H_2$ and CO versus ethylene. However, the angular profiles for $H_2$ and CO are assumed to be the same for all of their desorption states.

## 3. Results

**1. CO and H Coadsorption on Fe(100).** On Fe(100) saturated with one monolayer of adsorbed atomic hydrogen (Fe(100)–H), adsorbed CO induces new low-temperature $H_2$ desorption states[12] (Figure 1). In the absence of CO, hydrogen desorbs in two states only; the $\beta_2$ state appears first, displays second-order kinetics, and saturates at $^1/_8$ ML with a peak temperature $T_p$ of 390 K. As the hydrogen coverage is increased above $^1/_8$ ML, the $\beta_1$ state grows in and displays pseudo-first-order kinetics, since $T_p$ is invariant at 290 K with respect to coverage. An activation energy of 16.8 ± 0.6 kcal/mol and a second-order preexponential of $10^{-2.5\pm0.4}$ cm$^2$/s were measured for the $\beta_1$ state at $\Theta_H = 0.66$, the hydrogen coverage at the peak desorption rate. The total hydrogen coverage at saturation is 1.0 ± 0.1 ML. Similar pseudo-first-order desorption of $H_2$ from W(100) has been ascribed to adatom–adatom lateral interactions,[14] rather than hydrogen desorption being a true first-order process.

When 0.25 ML or less of CO is adsorbed on Fe(100)–H, a distinct new $H_2$ desorption state, $\gamma_2$, appears near 200 K. The activation energy for desorption of $\gamma_2$ hydrogen is approximately 12 kcal/mol, assuming the same preexponential factor for $\beta_1$-$H_2$; $H_2$ desorption in the $\gamma_2$ state thus is destabilized by approximately 5 kcal/mol by the presence of CO. In addition to the appearance of the $\gamma_2$ state, the two $\beta$-$H_2$ desorption states are broadened and shifted down in temperature, indicative of perturbation of the kinetics of recombination *via* these reaction channels. Another CO-induced $H_2$ desorption state, $\gamma_3$, is present for CO coverages above 0.25 ML; for a CO saturation coverage of $^1/_2$ ML the $\gamma_3$ state is quite sharp and exhibits a peak temperature of 254 K. No more than 0.1 ML of hydrogen is displaced by the postadsorption of CO to saturation on Fe(100)–H; hydrogen may not actually be displaced by CO, but the angular distributions and velocities of $H_2$ may be altered by postadsorbed CO, and thus coverages determined by TPD using $T_s^{1/2}$ corrections may be too low. However, when CO is adsorbed prior to $H_2$ exposure, the hydrogen saturation coverage drops monotonically with increasing CO coverage and no $\gamma$-desorption states result. For a CO saturation precoverage of 0.5 ML, hydrogen will not adsorb.

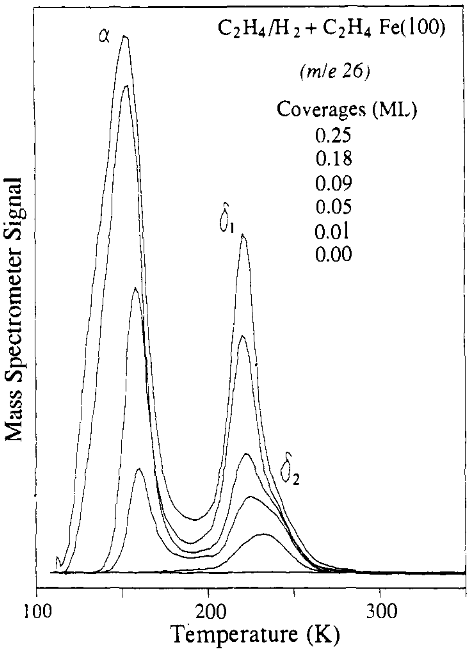

**Figure 2.** Temperature-programmed reaction spectra of $C_2H_4$ from H-presaturated Fe(100) for various $C_2H_4$ exposures. Heating rates are approximately 10 deg/s.

Although CO dissociates on Fe(100), it does so at temperatures high enough that CO dissociation should have no effect on the desorption of $H_2$ when the two species are coadsorbed. X-ray photoelectron spectroscopy (XPS) results of Benziger and Madix[17] as well as those of Brundle[18] indicate that CO dissociates only slowly at 300 K. Similarly, Moon et al. have reported that CO dissociation occurs only above 400 K.[19] The effects of CO on $H_2$ desorption from Fe(100) thus appear to be attributable to coadsorbed molecular CO.

The occurrence of new low-temperature desorption states of $H_2$ induced by CO coadsorption indicates that a mixed adlayer is formed.[3-5] This result is consistent with the behavior on other surfaces; Fe(100) is an open surface and mixed CO–H adlayers are typically formed on other open surfaces,[3-5] e.g. Ni(100),[20] Rh(100),[21] and W(100).[22] In contrast segregated structures are typically formed on close-packed surfaces,[3-5] i.e. Rh(111),[23] Ru(001),[24] and the (111) faces of Ni and Pt.[25] Additionally, the total coverage of H (1 ML) plus CO ($^1/_2$ ML) at CO saturation is too high to be explained by segregation of H and CO into islands. Even if CO and H segregation could lead to compression of H adatoms into regions with $\Theta_H > 1$ ML, which has no precedent among other CO and H coadsorption systems,[3-5] it is unlikely that the resulting CO saturation coverage on Fe(100)–H of 0.53 ML would be as close to its reasonably high clean-surface coverage of 0.58 ML. No adsorbate-induced LEED patterns were observed for the coadsorbed system. However, the $\gamma_2$ hydrogen state apparently results from a local CO coverage of ≤0.25 ML, since the population of the $\gamma_2$ state is a maximum at a global CO coverage of $^1/_4$ ML.

**2. Reactions of Ethylene on Fe(100)–H.** Ethylene reacts to

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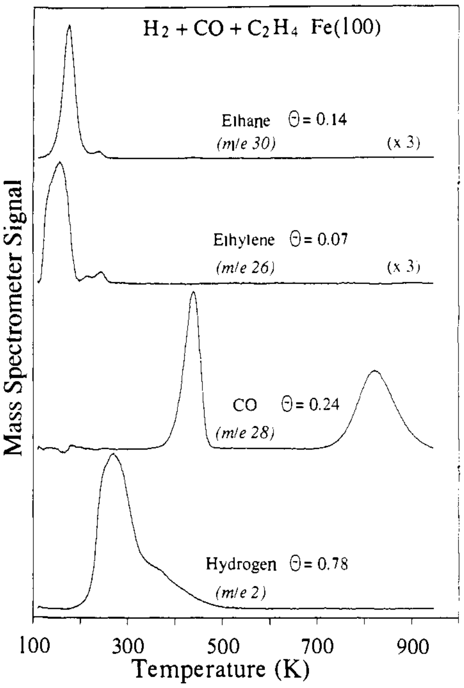

**Figure 3.** Temperature-programmed reaction spectra following the adsorption of 0.24 ML of CO onto H-presaturated Fe(100) with a post-exposure of $C_2H_4$ to saturate the surface. For each TPRS trace contributions from mass spectral fragments of products other than that designated have been subtracted. The heating rate is approximately 10 deg/s.

form stable ethyl ($C_2H_5$) groups on Fe(100)-H.[1] Three ethylene states are present in TPRS; the $\alpha$ state at 150 K arises from molecular desorption (Figure 2). The two $\delta$ states at 220 and 240 K are due to $\beta$-hydride elimination of ethyl groups formed, as evidenced by H-D exchange and kinetic isotope effects for $C_2H_5$, $CD_2CHD_2$, and $C_2D_5$.[1,45] The $\delta_2$ state saturates first at $\approx$0.01 ML, and it is attributed to defects. The saturation coverage of ethylene is 0.25 ± 0.05 ML. No decomposition of $C_2H_4$ occurs on the Fe(100)-H surface, and the desorption of $H_2$ is unaffected by ethylene since virtually all the ethylene has desorbed prior to the temperature at which hydrogen evolution begins from the clean surface. Other than trace amounts of ethane ($\leq$0.0007 ML), the only gas-phase products observed were hydrogen and ethylene.

**3. CO-Induced Ethane Formation on Fe(100)-H. a. CO Adsorbed before $C_2H_4$.** The adsorption of CO onto Fe(100)-H prior to the adsorption of ethylene results in the formation of up to 0.14 ML of ethane (Figure 3). The H atom stoichiometry for the data shown in Figure 3 indicates that the H adatom consumption of 0.22 ML is approximately 80% of that required to form the amount of ethane estimated from the desortion yield. Although increased sensitivity to $H_2$ cannot be definitely ruled out (i.e., by altered velocities and/or angular distributions) this difference places an error limit of ±25% on the stated yields.

The ethane product is evolved with a peak temperature of 170 K, well below the temperature of $\beta$-hydride elimination to form ethylene on the CO-free surface. Thus, CO must promote the reductive elimination step to form ethane rather than stabilize the ethyl groups to higher reaction temperatures, where reductive elimination of ethane might readily occur. The $H_2$ desorption spectrum in Figure 3 shows no sign of the $\gamma_2$ state, which is quite distinct at this coverage of CO on Fe(100)-H in the absence of coadsorbed ethylene. The disappearance of this state suggests that the $\gamma_2$ state is directly responsible for the formation of ethane. The maximum yield of 0.14 ML of ethane is achieved at a CO coverage near 0.2 ML (Figure 4). This result also points toward direct involvement of the $\gamma_2$ state of hydrogen, since the maximum population of the $\gamma_2$ state of $\approx$0.15 ML occurs in this range of CO coverage.

As discussed above, CO dissociates on otherwise clean Fe(100), but the rate of dissociation is only significant at temperatures above 300 K.[17-19] We thus infer that it is molecularly adsorbed CO which induces the formation of ethane at 170 K; the process and/or products of CO dissociation appear to play no role in ethane formation.

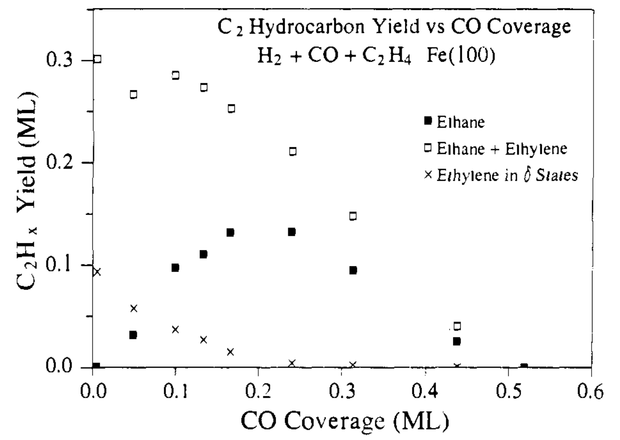

**Figure 4.** Ethane yield (■), total $C_2$ (ethane plus ethylene) yield (□), and ethylene yield in $\delta$ states (×) as a function of the coverage of adsorbed CO. CO was adsorbed onto H-presaturated Fe(100) prior to a saturation ethylene exposure.

The ethane yield rises almost linearly with $\theta_{CO}$ at CO coverages below 0.15 ML; it then passes through a maximum and falls to zero at CO saturation (Figure 4). Each CO thus has an equal probability of inducing ethane formation at low $\theta_{CO}$. However, the yield passes through a maximum and decreases at high CO coverages due to site blocking by CO; both the ethane yield and total $C_2$ (ethane plus ethylene) yield drop because CO blocks ethylene adsorption on the surface. Interestingly, the total yield falls very little up to CO coverages of 0.15 ML, suggesting that CO and $C_2H_4$ do not directly compete for binding sites in this coverage range. Other possible reasons for the constancy of the ethylene postsaturation coverage with low CO coverages are not supported by experimental results. For instance, CO does not appear to stabilize molecular $C_2H_4$, since the desorption temperature of the ethylene $\alpha$ state does not increase. Another possibility is that ethyl groups may form upon adsorption of $C_2H_4$ in the presence of CO. This could lead to enhanced $C_2H_4$ adsorption if ethyl-ethylene repulsion is weaker than that of ethylene-ethylene. However, kinetics of ethane formation based on peak shapes indicate that this is unlikely (see below).

The yield of ethylene in the $\delta$ states is reduced rapidly as CO coverage increases (Figures 3 and 4), and is nearly zero for CO coverages above 0.25 ML. The $\delta$ states arise from the $\beta$-hydride elimination of ethyl groups (Section 3.2); the drop in their population in the presence of CO is consistent with the promotion of the competing reaction of ethane formation by CO. The alternative explanation that CO inhibits the formation of the ethyl groups is unlikely, since the reaction to form ethane proceeds readily when ethyl groups have been formed and isolated by annealing to 175 K prior to the adsorption of CO. In addition, an ethyl group is a logical intermediate in the pathway for ethane formation, and the inhibition of ethyl formation by CO would thus be inconsistent with the observed promotion of ethane formation by CO. The accuracy of our values for ethane yield and for the coverage of ethyl groups attained when no CO is coadsorbed is too low for us to determine whether CO enhances the formation of ethyl groups. However, CO clearly induces the reductive elimination of ethane. In the presence of CO the $\delta$-$C_2H_4$ states occur at approximately the same temperature as when CO is absent. The $\delta_1$ state appears to be shifted downward by CO, but reliable quantification of $\delta$ state kinetics in the presence of CO is not possible, since cracking of the ethane product contributes significantly to the signal for $m/q$ values used to monitor ethylene. Subtraction of this contribution leads to a large uncertainty in peak temperatures and line shapes, especially at high CO coverages where the yield of $\delta$-$C_2H_4$ is small relative to $C_2H_6$. A small $\delta$-$C_2H_4$ state at 240 K (Figure 3) persists up to CO coverages of

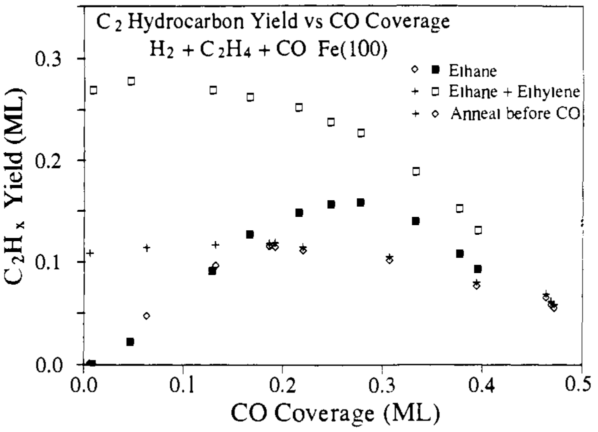

**Figure 5.** Ethane yield (■) and total ethane plus ethylene yield (□) as a function of the coverage of postadsorbed CO. CO was adsorbed after a saturation ethylene exposure on H-presaturated Fe(100). Also shown are ethane yield (◇) and total $C_2$ (ethane plus ethylene) yield (+) for the same dosing order, but the ethylene covered surface has been annealed to 175 K prior to CO adsorption in order to form ethyl groups and desorb molecular ethylene.

0.43; this may indicate a reduced propensity for hydrogenation of the $\delta_2$ state, which desorbs at this temperature in the absence of CO. There is no evidence, however, that the $\delta$ states are shifted to higher temperatures by CO, thus CO does not appear to inhibit the $\beta$-hydride elimination of $C_2H_{5(a)}$. Since the adsorbate layers do not induce any LEED patterns, we cannot suggest specific structures and interactions responsible for CO-induced ethane formation. However, a discussion of the interactions in the adlayer that are likely to be responsible are presented in Section 4.1.

**b. CO Adsorbed after $C_2H_4$.** Ethane formation is also induced by CO when it is adsorbed following $C_2H_4$. The yield of ethane as a function of CO coverage again passes through a maximum at 0.3 ML of CO, which yields 0.17 ML of ethane (Figure 5, filled squares). In addition to ethane, some $C_2H_4$ is evolved at even the highest CO coverages, as indicated by the sum of the ethane and ethylene yield (open squares in Figure 5). The total of the $C_2$ products evolved stays constant at low coverages of CO, but drops for $\theta_{CO} \geq 0.2$. Similar results are obtained if CO is adsorbed onto a surface covered with ethyl groups, formed by annealing an ethylene saturated Fe(100)-H surface to 175 K to isolate the $\delta$ state. The maximum ethane yield is lower in this case, however; 0.12 ML of ethane is formed at a CO coverage of 0.2 ML (Figure 5, diamonds). At CO coverages above 0.2 ML no ethylene is evolved, so all the ethyl groups are converted to ethane. Thus the total $C_2$ (ethane plus ethylene) yield (Figure 5, crosses) equals the ethane yield at high CO coverages.

The reduction of ethane yield at high CO postcoverages on the ethylene-presaturated Fe(100)-H surface may arise from the displacement of some ethylene by adsorbing CO (Figure 6a). Ethylene desorption occurs rapidly upon raising the crystal temperature when 0.4 ML of CO is postadsorbed onto $C_2H_4$-saturated Fe(100)-H (Figure 7a, solid line); ethylene desorption also occurs rapidly from $C_2H_4$-saturated Fe(100)-H when no CO is coadsorbed. That ethylene is so weakly bound at saturation suggests that it may be displaced by CO at the dosing temperature. In contrast to ethylene, ethane evolution following CO postadsorption on the ethylene presaturated surface does not become significant until above 120 K, even for $\theta_{CO} = 0.4$, the highest CO coverages attained (Figure 7b, dotted line). The rate of ethane formation at the dosing temperature does not appear sufficient to lead to ethane displacement by CO. However, the reduced ethane yield for high CO postcoverages onto ethyl-precovered Fe(100)-H (i.e. the ethylene precovered surface which has been annealed to 175 K to form ethyl groups before the adsorption of CO) may arise from CO-induced displacement of ethane (Figure 6b). When 0.4 ML of CO is postadsorbed onto an ethyl-precovered surface the evolution of ethane occurs much more rapidly (Figure 7c, dashed line) than when 0.4 ML of CO is adsorbed onto the ethylene-precovered surface which has not been preannealed to form ethyl groups (Figure 7b, dotted line). No ethylene desorption is apparent in the temperature-programmed reaction following the post-adsorption of 0.4 ML of CO onto the ethyl-precovered surface, but displacement of ethylene by CO in this experiment cannot be definitively ruled out.

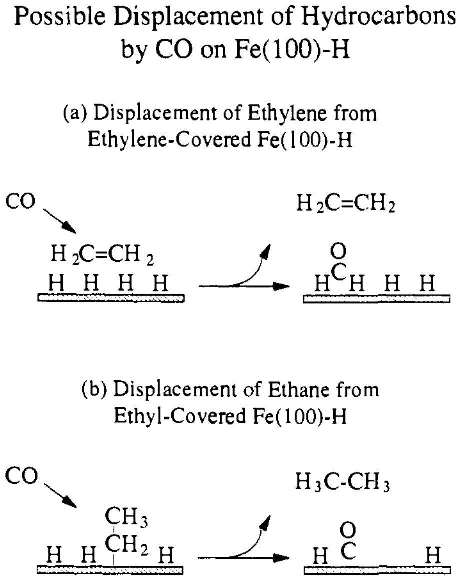

**Figure 6.** Illustrations of the possible displacement of hydrocarbons by the adsorption of CO on Fe(100)-H at 110 K. In part a CO displaces ethylene from the ethylene-precovered Fe(100)-H surface. In part b CO displaces ethane from ethyl-precovered Fe(100)-H, which was prepared by annealing the ethylene-precovered surface to 175 K.

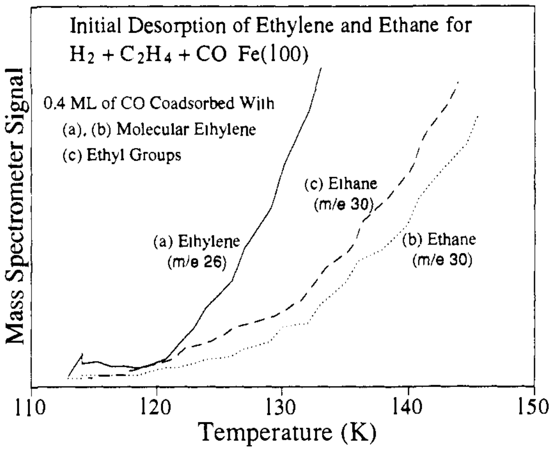

**Figure 7.** Initial desorption of (a) ethylene (*m/q* 26, solid line) and (b) ethane (*m/q* 30, dotted line) during temperature-programmed reaction following the adsorption of 0.4 ML of CO on an Fe(100)-H surface presaturated with ethylene. Curve c shows the evolution of ethane (*m/q* 30, dashed line) following the adsorption of 0.4 ML of CO on an ethylene saturated Fe(100)-H surface which has been annealed to 175 K before CO adsorption in order to form ethyl groups and desorb molecular ethylene. Ethylene desorption in part a has been corrected for mass spectral cracking of the ethane product and has been corrected for the relative mass spectrometer sensitivities of ethylene at *m/q* 26 and ethane at *m/q* 30. Heating rates are approximately 10 deg/s.

**c. Qualitative Comparison of Ethane Formation Kinetics.** The kinetics of the evolution of ethane changed only slightly when the order of adsorption of CO and $C_2H_4$ was reversed (Figure 8). For the same CO coverage and similar ethane yields the peak shape for ethane evolution shows a high-temperature shoulder when $C_2H_4$ is adsorbed first (dotted curve) that is much smaller when CO is adsorbed first (solid curve). This difference may originate from preferential binding of $C_2H_4$ at defects when it is adsorbed first, with CO binding at these sites, and thus blocking them, when the order of adsorption is reversed. At defects the more strongly held

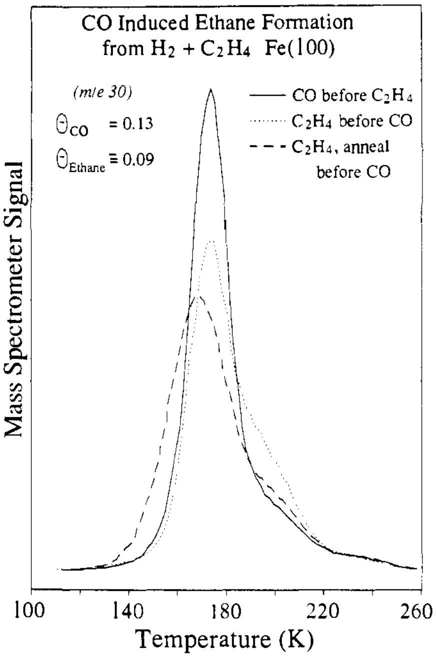

**Figure 8.** Ethane temperature-programmed reaction traces for CO adsorbed prior to ethylene (solid line), subsequent to ethylene (dotted line), and subsequent to ethylene with a preanneal to 175 K to form ethyl groups (dashed line), all on H-presaturated Fe(100). The CO coverage in each case is 0.13 ML, with approximately equal ethane yields of 0.09 ML. Heating rates are approximately 10 deg/s.

ethyl groups may possess a higher barrier to the reductive elimination of ethane.

However, when ethyl groups are created by annealing to 175 K prior to CO adsorption (dashed curve) a significant change in the shape of the ethane peak occurred; the peak temperature shifted down about 6 K and the peak broadened. When CO and *molecular* $C_2H_4$ are coadsorbed at 110 K the onset of ethane evolution occurs in the temperature range where ethyl group formation occurs.[1] This fact and the higher evolution temperature of ethane when CO is coadsorbed with molecular $C_2H_4$ rather than with $C_2H_5$ suggest that the kinetics of ethane formation are coupled with the formation of ethyl groups when CO is coadsorbed with molecular $C_2H_4$. However, when CO is postadsorbed onto an ethyl-precovered surface, the kinetics of ethane formation should be indicative of the reductive elimination step only.

Approximate activation energies, *E*, for ethane formation were determined from plots of ln (rate) versus $1/T$ at the leading edge, where variations in coverage are minimal. The resulting activation energy is 5.3 kcal/mol when CO is adsorbed onto a surface which has been preannealed to form ethyl groups. Values of 6.1 and 6.5 kcal/mol were obtained for the unannealed surface when CO was adsorbed after or before $C_2H_4$, respectively. The reaction barriers are thus not significantly different in the three cases.

**d. Ethane Formation at Reduced H Coverages.** In order to further probe the structural and phase properties of the CO–H adlayer which are responsible for ethane formation, a series of experiments was performed at reduced hydrogen coverages. In all subsequent discussion ethane yields refer to experiments in which CO was adsorbed prior to $C_2H_4$ and, except where noted, subsequent to $H_2$; all species were adsorbed at a temperature of 110 K. Note that the amount of $H_2$ evolved during temperature-programmed reaction depends on the initial H coverage as well as the extent of ethane formation and ethylene decomposition. The initial H coverage was thus determined by performing a separate $H_2$ TPD immediately before each ethylene hydrogenation experiment, with the same hydrogen exposure used in both. Hydrogen coverage quoted for a set of TPRS experiments is the average over all of the experiments in the set; variations from the average were less than 3% for any given experiment.

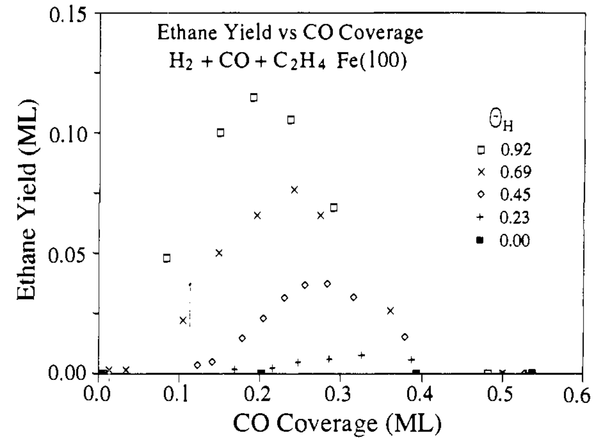

**Figure 9.** Ethane yield as a function of CO coverage for CO adsorbed onto H-precovered Fe(100) prior to a saturation ethylene exposure. The H precoverages used were 0.92 (□), 0.69 (×), 0.45 (◇), 0.23 (+), and 0.00 ML (■).

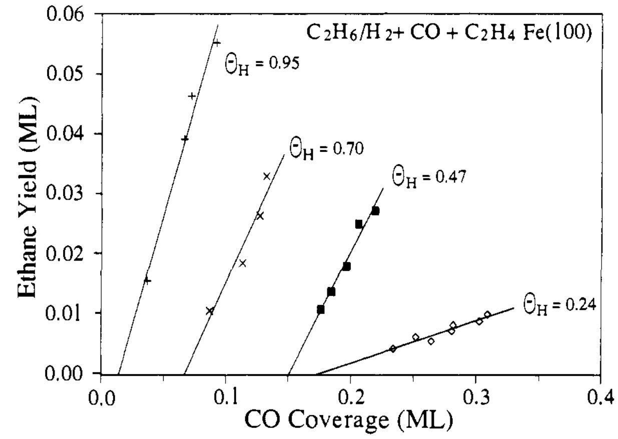

**Figure 10.** Ethane yield as a function of CO coverage for CO adsorbed onto H-precovered Fe(100) prior to a saturation ethylene exposure. The H precoverages were 0.95 (+), 0.70 (×), 0.47 (■), and 0.24 ML (◇). CO coverages were varied between the threshold and that producing the maximum ethane yield.

The ethane yield as a function of CO coverage from zero to saturation was determined for five initial $H_{(a)}$ coverages between 0 and 0.92 ML (Figure 9). Except for $\Theta_H = 0.0$, where no ethane is formed, the production of ethane generally requires a threshold CO coverage. The ethane yield then rises smoothly with CO coverage before passing through a maximum and falling to zero at a presaturation coverage of CO. As the initial hydrogen coverages were decreased, the CO coverages corresponding to both the threshold for ethane formation and the maximum ethane yield increased.

That a CO threshold coverage exists and that it increases as the precoverage of H decreases implies that the H adlayer must be compressed and/or restricted into regions with a critical local coverage in order for ethylene hyrogenation to occur. Accurate values for these threshold CO coverages as well as the ethane yield per CO molecule were found at four hydrogen precoverages (Figure 10). CO coverages were varied at more closely spaced intervals between the threshold and those producing the maximum ethane yield. The ethane yield increased linearly with $\Theta_{CO}$ in this CO coverage range; the threshold CO coverage and the number of ethane molecules formed per CO molecule (slope) were extracted from a linear least-squares fit and are plotted as a function of H precoverage in Figure 11. The threshold CO coverage, $\Theta_{CO,th}$, required for $C_2H_6$ formation varies linearly with the value of the H precoverage approximately according to $4\Theta_{CO,th} + \Theta_H = 1$.

However, for a given CO coverage the H coverage in the "threshold" adlayer, i.e. $\Theta_H = 1 - 4\Theta_{CO}$, is *lower* than the saturation coverage of H on a surface precovered with the same amount of CO. For instance, the threshold molecular CO coverage

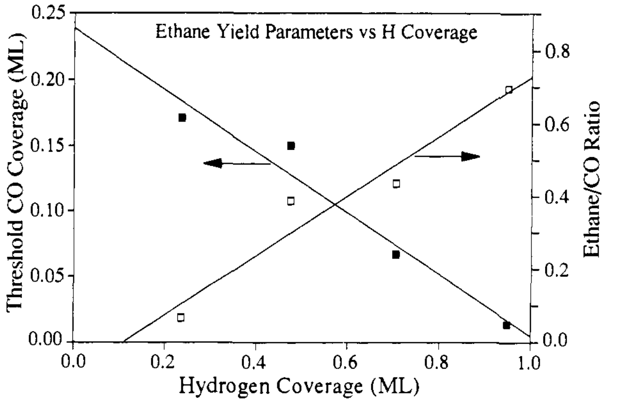

**Figure 11.** CO postcoverages at the threshold for ethane formation (■) and the ethane yield per postadsorbed CO molecule (□), both as a function of H precoverage.

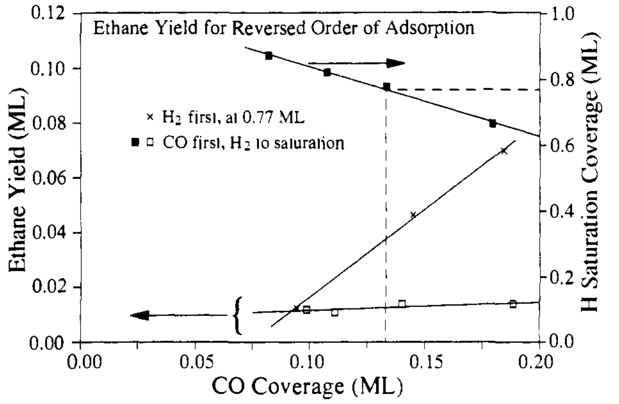

**Figure 12.** Demonstration of inequivalent ethane yields at $\theta_{CO} = 0.13$ and $\theta_H = 0.77$ for opposite orders of CO and $H_2$ adsorption prior to a saturation exposure of ethylene. Hydrogen post-saturation coverages (□) and ethane yield (□) are shown as a function of CO precoverage. Also shown is the ethane yield for an H precoverage of 0.77 ML (×) with varying CO postcoverages. An H postsaturation coverage (■) of 0.77 ML is obtained with a CO precoverage of 0.13 ML (horizontal dashed line); the ethane yield for the opposite orders of adsorption are thus compared at this CO coverage (vertical dashed line).

in the zero $\theta_H$ limit is 0.25 ML, yet at this same CO precoverage (dosed at 110 K) the saturation coverage of postadsorbed hydrogen is 0.4 ML.[1] Thus, for CO coverages greater than zero on the $H_2$ predosed surface, the "threshold" adlayer is not saturated with H.

In order to pursue this difference further, ethylene hydrogenation yields were determined for the same total CO and H coverages, but with the opposite order of adsorption of $H_2$ and CO. If CO must adsorb on top of a locally concentrated H adlayer in order to induce ethane formation, the amount of ethane formed when $H_2$ is adsorbed first should be considerably greater than that formed when CO is preadsorbed, since in the latter case CO will block $H_2$ adsorption in its vicinity. The hydrogenation yield for CO adsorbed at 110 K on top of 0.77 ML of H (Figure 12, crosses) and the hydrogenation yield for CO adsorbed prior to a saturation hydrogen dose at 110 K (open squares) were determined. For the latter case the CO precoverages were chosen so that the H saturation coverages would bracket the 0.77 ML value used when hydrogen was adsorbed first. The H saturation coverages as a function of CO precoverage (filled squares in Figure 12) were determined independently; all three curves in Figure 12 were obtained by alternating among the different experiments.

Hydrogen saturation coverages and ethane yields for a given CO precoverage followed by saturation by H are shown in Figure 12 as filled and open squares, respectively. Also shown is the ethane yield for an initial hydrogen precoverage of 0.77 ML postdosed with varying amounts of CO. The ethane yield at $\theta_H = 0.77$ was a factor of 3 larger when hydrogen was preadsorbed than when it was postadsorbed at the same coverage of 0.13 ML of CO (see vertical dashed line). The vertical line drawn at $\theta_{CO} = 0.13$ through the plots of ethane yield for pre- and postadsorbed $H_2$ indicates an ethane yield of 0.039 ML for $H_2$ preadsorption compared to the yield of 0.014 ML for $H_2$ postadsorption.

## 4. Discussion

**1. Mechanism of Activation by CO. a. Effect of CO on Elementary Reaction Steps.** The most likely origin of the promotion of ethylene hydrogenation by CO is the destabilization of the Fe–H bond. Coadsorbed CO clearly destabilizes H adatoms toward desorption, leading to the formation of $\gamma$-$H_2$ desorption states. As noted in Section 3.3, ethane is evolved at temperatures below those for $\beta$-hydride elimination of ethylene from adsorbed $C_2H_5$ on the CO-free Fe(100)–H surface. It is thus the promotion of the reductive elimination reaction by CO and not the inhibition of the competing $\beta$-hydride elimination reaction that results in ethane formation. The temperature at which ethylene is evolved supports this conclusion, since there is no evidence of a CO-induced shift to higher temperatures. The decrease in the yield of $C_2H_4$ from $\beta$-hydride elimination in the presence of CO is consistent with the promotion of the competing reductive elimination of ethane by CO. The $\gamma_2$-$H_2$ state seems to be directly involved in ethane formation, since this state appears to be reacted away upon the adsorption of $C_2H_4$, and the maximum yields of both $\gamma_2$-$H_2$ and ethane are obtained at a CO coverage of 0.20–0.25 ML.

When ethylene is adsorbed on Fe(100)–H *without* coadsorbed CO, no ethane is formed, and all ethyl groups react via $\beta$-hydride elimination with an activation barrier of 13.2 kcal/mol and a preexponential of $10^{13.4}$ $s^{-1}$.[1] The activation barrier for reductive elimination of ethane in the absence of CO must then be on the order of 13 kcal or greater (assuming equal preexponential factors), since the rate of ethane formation is insignificant compared to that of $\beta$-hydride elimination. The activation barrier to ethane formation in the presence of CO is approximately 5–6 kcal/mol; thus CO reduces the activation barrier to reductive elimination by approximately 7–8 kcal/mol. The observed CO-induced destabilization for $\gamma_2$-$H_2$ of approximately 5 kcal/mol appears to be the major factor responsible for ethane formation, but given the uncertainties in activation energies for $\gamma_2$-$H_2$ desorption and for ethane formation both with and without coadsorbed CO, other effects, such as modification of the Fe–$C_2H_6$ bond, may also play a role.

**b. Origin of CO Activation of H Adatoms.** The fact that CO must be adsorbed above a threshold coverage on H-predosed surfaces strongly suggests that adsorbed H must be compressed into locally concentrated regions onto which CO then adsorbs in order to produce ethane. Such behavior is consistent with the necessity for formation of the $\gamma$-$H_2$ state. Further, ethane formation in the mixed CO–H adlayer is most efficient as the precoverage by hydrogen approaches saturation (Figure 10). Clearly, locally saturated regions are most effectively perturbed by adsorbed CO to produce ethane. Quantitatively, the ethane yield depends on the CO–H phase behavior, as evidenced by the differing results obtained when the order of adsorption of CO and $H_2$ is reversed (Figure 12). The details of this phase behavior have yet to be determined.

The suggestion that CO must adsorb into regions locally concentrated with $H_{(a)}$ in order to activate H adatoms toward ethane formation is consistent with the conclusion that a mixed adlayer is formed when CO is adsorbed onto the H-presaturated surface (Section 3.1). This implies that effectively a short-range repulsion between CO and H adatoms is the source of H activation. The same inference has been made regarding $\gamma$-$H_2$ desorption states induced by postadsorbed CO.[12] There are several possible origins of the short-range CO–H interaction, the first of which is direct repulsion. Currently, the binding sites for H adatoms on Fe(100) and for CO adsorbed onto Fe(100)–H are not known. However, on H-presaturated Ni(100)[3] and Rh(100)[21] surfaces the binding site for H is the 4-fold hollow and for CO it is the atop site. Assuming the same site configuration for CO on Fe(100)–H *maximizes* the resulting CO–H distance. Using literature values for covalent radii[26] of 1.25 Å for Fe, 0.77 Å for C, and 0.37 Å for H gives a C–H separation distance between adsorbed CO and H of 2.7 Å. This distance is less than 3.0 Å, which is the sum of van der Waals radii[26] of C (1.7 Å) and of H (1.3 Å); direct Pauli repulsion between CO and H may then be a means by which CO activates H adatoms.

Electrostatic repulsion may also be a factor. Work function measurements for $H_2$ adsorption on Fe(100) indicate that the work function increases as $\Theta_H$ increases.[27] Molecular CO also increases the work function of Fe(110)[28] and of Fe(poly).[29] Although analogous studies for CO on Fe(100) have not been made, the same result is expected on Fe(100). Both H and CO adspecies thus withdraw charge from the surface and would be mutually repellent due to electrostatics. On the basis of effective medium calculations, Norskov et al.[30-32] have concluded that electrostatic interactions may be responsible for many cases of stabilization and destabilization of coadsorbed species on transition-metal surfaces. Also, Hardegree et al. have shown that electrostatic repulsion may be the dominant interaction mechanism between sulfur and CO coadsorbed on Ni(100) for interadsorbate distances greater than the sum of van der Waals radii.[33]

Through-surface effects may also be a major contributor to the activation of H adatoms by CO. The large reduction in $\nu$(CO) from 2143 to 1250 $cm^{-1}$ upon adsorption of CO onto clean Fe(100)[34,35] and the propensity of CO to dissociate on this surface are indicative of a strong adsorbate–metal interaction. H adatoms also interact strongly with Fe(100), as reflected by the Fe–H bond energy of 60 kcal/mol.[12] These strong interactions imply that metal–adsorbate orbital mixing is extensive. Since CO and H must undoubtedly share iron atoms in bonding when CO is adsorbed on Fe(100)–H, a CO-induced Fe(100) restructuring of metal electronic states would not have to be long-ranged in order for the Fe–H bond to be affected. Analogies exist in homogeneous transition-metal complex chemistry, where CO may strongly destabilize other ligands, especially those trans to itself, due to its strong $\pi$-acceptor character.[36,37] Similar, but longer-ranged through-metal interactions between CO and H have been probed in calculations by Ruckenstein and Halachev for species adsorbed onto a Rh(111) cluster.[38] They have found that the interaction energy is repulsive for CO–H separation distances ranging from one to two times the Rh–Rh nearest-neighbor distance.

**c. Other Interactions in the Adlayer.** The ability of CO to promote ethylene hydrogenation may arise partly from its versatility in binding to metal surfaces. CO has been found to occupy atop and 2-fold bridge sites as well as hollow sites on various metals at various coverages.[39] On the H-free Fe(100) surface CO adsorbed at coverages below 0.25 ML has been found to "lie down", probably in a 4-fold hollow site.[34,35,40] CO adsorbed in excess of 0.25 ML on Fe(100), however, is bound in 2-fold bridge and atop sites, with the C–O bond axis normal to the surface.[34,35] Even though H adatoms may occupy the 4-fold hollow binding sites, where CO would preferentially adsorb, CO may alter its binding configuration to minimize CO–H repulson and yet still bond strongly with the metal. Consequently, strong repulsion between CO and H can occur in the adlayer without displacement of $H_2$ at low temperatures. A CO–Fe bond of moderate strength may be crucial for promotion of the reaction, since a weakly bound adsorbate may not decrease the Fe–H bond energy enough. Additionally, a more strongly bound adsorbate may have too great of a preference for the same binding site as $H_{(a)}$, and thus displace $H_2$ from the surface.

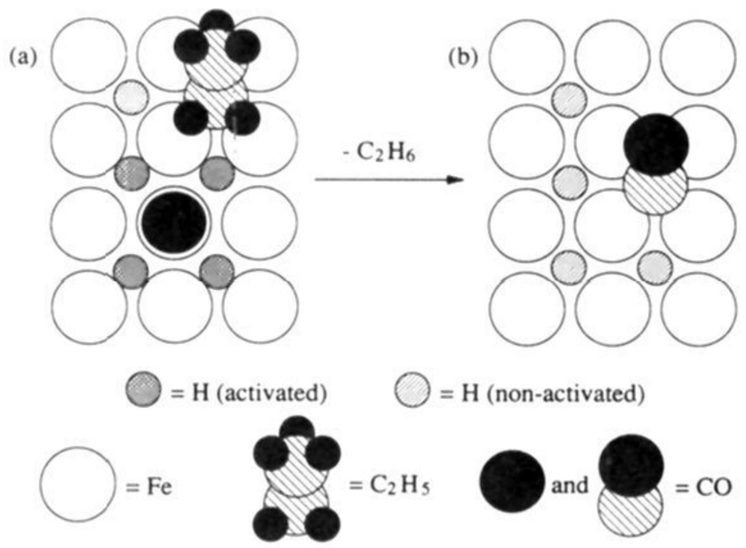

**Figure 13.** Hypothetical adlayer structures (a) prior to and (b) subsequent to the reductive elimination of ethane on Fe(100)–H.

Ethane formation induced by coadsorbed CO is most efficient on the H-presaturated surface. Since vacancies arise in the adlayer when "activated" H adatoms react with ethyl groups to form ethane, as shown hypothetically in Figure 13, CO may move into the vacant sites causing a structural relaxation which "deactivates" other H adatoms which were strongly perturbed by CO. Our experimental value for the ratio of ethane formed per CO adsorbed is 0.7 ± 0.2 for the low $\Theta_{CO}$ limit on H-presaturated Fe(100) (Figure 11). The lack of adsorbate-induced LEED patterns also precludes a definitive attribution of the CO promotion effect to isolated rather than island CO molecules. Shifts in the CO stretching frequency as a function of CO coverage should give insights into the degree of dipole coupling in the CO adlayer, and thus allow distinction between island and isolated CO at low CO coverages on Fe(100)–H. These vibrational studies are currently planned in this laboratory.

**2. Diffusional Barriers in the "Threshold" Adlayer.** As discussed above, the H and CO coverages at the threshold for ethane formation suggest that CO must adsorb into regions *locally* concentrated with hydrogen, in order for ethane formation to occur (Section 3.4) (Figure 12). However, for a given CO postcoverage the H precoverage in the "threshold" adlayer, determined by $\Theta_H = 1 - 4\Theta_{CO}$, is considerably lower than the H postcoverage attained by a saturation dose of $H_2$ on a surface precovered with the same amount of CO. Presumably, the adlayer resulting from CO postadsorption onto the H-precovered surface to coverages just above threshold (i.e. $4\Theta_{CO} + \Theta_H > 1$) is in a higher potential energy configuration than that formed with CO preadsorbed with the same adlayer composition. Some postadsorbed CO may bind in regions with $\Theta_{H,loc} = 1.0$, whereas preadsorbed CO would exclude postdosed hydrogen from adsorption from its vicinity; shorter CO–H distances and greater CO–H repulsion would thus result for postadsorbed versus preadsorbed CO. The H adlayer appears to be in a higher energy configuration when CO is postadsorbed since only *post*adsorbed CO significantly lowers the activation barrier to $H_2$ desorption (by inducing $\gamma$-$H_2$ desorption) and promotes H reactivity toward ethane formation.

The phenomenon above may be due to diffusional barriers in the "threshold" adlayer formed when CO is postadsorbed onto surfaces at hydrogen coverages below saturation. These barriers may inhibit relaxation of the "threshold" adlayer into lower energy structures with larger CO–H distances and reduced H adatom reactivity. The requirement that $4\Theta_{CO} + \Theta_H > 1$ for ethane formation suggests that one postadsorbed CO molecule is required

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for every four vacancies in the H adlayer in order to prevent relaxation of "activated" H adatoms, formed when postadsorbed CO molecules above the threshold coverage bind within regions locally concentrated with H.

**3. Implications toward CO-Induced H Reactions on Other Surfaces.** The enhanced reactivity displayed by $H_{(a)}$ in the presence of CO may not be entirely specific to Fe(100), but it certainly depends on the phase behavior of the CO-H adlayer. In particular, CO adsorbed on top of the H saturated surface must form a mixed adlayer in order to attain the short CO-H distances which are required for activation of $H_{(a)}$. Conversely, segregated CO-H structures generally form on the close-packed faces of transition metals, e.g. fcc (111) and hcp (001).[3-5] In these cases CO adsorbed at 100 K compresses preadsorbed H into islands of saturation coverage and binds only outside of the H adatom islands at all CO coverages. Strong CO-H repulsion apparently results from the short interadsorbate distances on the close-packed surfaces, preventing CO from binding in the H-saturated regions. This behavior is not limited to CO; on Ru(001) the extent to which the saturation coverage of ethylene at 130 K is reduced by preadsorbed hydrogen implies that $C_2H_4$ would not adsorb on the surface at $\Theta_H = 1$.[7] This conclusion is based on the fact that $\Theta_{H,sat} = 0.85$ on Ru(001), and only a small amount of ethylene adsorbs at H saturation. Since neither CO[3-5] nor ethylene[7] appear to chemisorb in regions locally saturated with H on close-packed surfaces, CO should not induce hydrogenation reactions on these surfaces.

In contrast, CO adsorbed on an open transition-metal surface which has been presaturated with H forms mixed structures. Distinct low-temperature $H_2$ desorption states are induced by CO-H repulsion arising from short CO-H separations in the adlayer.[3-5]. Representative systems include CO and H coadsorption on the (100) face of the fcc metals Ni and Rh and the bcc metal W.[20-22] Hydrogenation reactions may or may not be induced by CO on these open faces, however, depending on the local CO coverages present in the adlayer. On Rh(100), for instance, CO adsorbed on top of the H-saturated surface forms islands at almost all CO coverages.[21] These islands have a local CO coverage of 0.5 ML on top of the H-saturated surface. Our result that a local CO coverage of 0.5 ML shuts off the pathway for ethylene hydrogenation by blocking ethylene adsorption suggests that H adatoms bound within CO islands on Rh(100) would not be available for hydrogenation reactions due to the high local CO coverages. Reactions of adsorbed H may be induced at the edges of the islands, where some of the "activated" H adatoms can still be accessed by incoming reactants. However, it is entirely possible that the CO phase behavior may be modified by the presence of preadsorbed ethylene, resulting in a lower $\Theta_{CO,loc}$. In this case postadsorbing CO after $C_2H_4$ could lead to significantly higher hydrogenation activity than when CO is adsorbed onto the H-saturated surface prior to ethylene adsorption. The importance of the surface phase behavior for surface reactions in which one species may act as an activating agent is evident from the study reported here.

**4. Analogies to Homogeneous Reactions.** A brief comparison to reactions of homogeneous transition-metal complexes is in order here, especially in view of the discussion of surface-complex analogies presented elsewhere in relation to the reactions of ethylene on Fe(100)-H in the absence of CO.[1] As discussed above, CO may weaken Fe-H bonding on the surface either through direct repulsion or through electronic effects mediated by the metal. Ligands have analogous effects on the reactivity of transition-metal complexes due to both steric and electronic effects. For example, steric interactions may dramatically weaken metal-ligand bond energies of alkyls[41] and olefins.[42,43] This reduction may translate into enhanced rates of reaction. For example, Doherty and Bercaw have determined that the rate of the migratory insertion of propylene into the metal-H bond of $(C_5Me_5)_2Nb(H)$(olefin) complexes is faster than that of ethylene.[44] Reduction of the Nb-propylene bond energy relative to that of ethylene due to steric repulsion raises the energy of the reactant and thus lowers the barrier to reaction. It is also of note that the hydrogenation activity of $RhCl(PPh_3)_3$ is greatly reduced when substituents less bulky than phenyl rings are substituted in the phosphine ligands.[45] We believe that the role of CO in promoting ethylene hydrogenation on Fe(100) is primarily to weaken Fe-H bonding. Steric repulsion between CO and H adatoms may play a role in this mechanism due to their close proximity on the surface.

The electronic effects of ligands are also well-documented, particularly for CO. As noted in Section 4.1.b, CO is a good $\pi$ acceptor, and thus withdraws electron density from the metal center due to extensive mixing of the vacant CO $\pi^*$ orbitals with occupied metal d orbitals.[36,37] This charge transfer reduces the ability of the metal atom to bind with other ligands, particularly one located trans to the CO. The effect is thermodynamic (referred to as a "trans influence"), since metal-ligand bond energies are reduced, and also kinetic (referred to as a "trans effect"), since the rate of ligand substitution at the coordination site trans to CO is enhanced.[36,37] A similar mixing of the CO $\pi^*$ orbital with metal surface wave functions may result in a weakening of the Fe-H bond on Fe(100). Since CO and H bind intimately in the mixed adlayer, the modification of the surface electronic structure by CO would have to be only short-ranged in order to explain the observed weakening of the Fe-H bond; i.e., it could be confined to a single metal atom to which CO and H both bind.

**5. Relation to Previous Surface Studies.** To the best of our knowledge there is no precedent in the surface science literature for the promotion of hydrogenation reactions by CO. In fact CO generally behaves as an inhibitor of surface reactions. Generally, the studies of the effects of CO have been restricted to systems where CO is coadsorbed with only one other species, e.g. hydrogen, ethylene, or benzene; thus the range of possible influences of CO or other coadsorbates has hardly been explored. For instance, we know of no previous UHV studies of the tertiary H-olefin-CO system, which is quite surprising, since the hydroformylation reaction is catalyzed by supported Co and Rh catalysts.[46]

A few cases have been documented which demonstrate the alteration of kinetics and selectivity for reactions by coadsorbed CO. On Ru(001) ethylene decomposes to form both acetylide (CCH) and ethylidyne ($CCH_3$), but the presence of coadsorbed CO greatly increases the acetylide:ethylidyne product ratio.[7] This difference has been interpreted in the context of a reaction mechanism for ethylidyne formation which proceeds from adsorbed ethylene through vinylidene ($CCH_2$), which then adds hydrogen to form ethylidyne, or dehydrogenates to yield acetylide. Due to CO-H repulsion, when CO is present on the Ru(001) surface during $C_2H_4$ decomposition, the adatom recombination temperature of the $H_{(a)}$ formed during ethylene decomposition is shifted down. Thus a lower surface coverage of H is available for reaction with the vinylidene intermediate to yield ethylidyne, resulting in a higher proportion of acetylide. Although the outcome of this reaction is the *inhibition* of a hydrogenation step by CO, the general role of CO as a source of destabilization of H is analogous to the mechanism operative in the promotion of ethylene hydrogenation on Fe(100) we report here.

Another case of a change in reaction selectivity by coadsorbed CO involves ethylidyne formation on Rh(100). As for Ru(001), ethylidyne formation from $C_2H_4$ on Rh(100) competes with the formation of acetylide.[10] In the absence of CO ethylene adsorbed at 300 K decomposes to form acetylide, with ethylidyne formation occurring only for ethylene coverages above 0.5 ML. However, on a Rh(100) surface precovered with 0.5 ML of CO, ethylene reacts at 300 K to form ethylidyne only.[9] This reactivity change can be viewed as site blocking by CO; the blocking of sites by

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(41) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(42) Reference 2, Chapter 3.

(43) Hartley, J. R. *Chem. Rev.* **1973**, *73*, 163.

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(45) Montelatici, S.; van der Ent, A.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1054.

(46) Wagner, F. S. In *Applied Industrial Catalysis*; Academic: New York, 1983; Vol. 2.

preadsorbed CO causes ethylene to react in the same way as it would at high coverages on Rh(100) in the absence of CO.

In fact, site blocking is the most general mechanism by which CO appears to modify surface reactivity. Another example is the inhibition of ethylidyne decomposition on Ru(001) by CO.[7,8] The desorption temperature of CO on an ethylidyne covered surface is higher than the temperature at which ethylidyne decomposes in the absence of CO. At higher coverages CO blocks sites for the decomposition of ethylidyne, thus stabilizing ethylidyne by approximately 30 K, until CO begins to desorb. Similar behavior occurs on a Ni(100) surface which has been prepared with adsorbed ethylene or fragments formed via ethylene decomposition (e.g. vinyl, acetylene, vinylidene, acetylide, and methylene) and is then postsaturated with CO at 100 K.[6] In the absence of CO low coverages of ethylene completely decompose on Ni(100), and molecular desorption occurs only after the decomposition pathway has been saturated. Postsaturation of CO onto Ni(100) at a low ethylene coverage blocks ethylene decomposition and leads to molecular desorption of almost all of the ethylene. If the ethylene adlayer is annealed so that partial decomposition to $C_2H_x$ fragments occurs, and then CO is dosed to saturation, the decomposition of the hydrocarbon fragments is inhibited until the CO begins to desorb. $C_2H_x$ fragments may thus be stabilized by up to 150 K by the presence of CO. However, in all of these cases saturation exposures of CO are required to completely inhibit hydrocarbon decomposition at temperatures below the onset of CO desorption.[6,8] The behavior of CO in previous surface studies as a reaction inhibitor thus contrasts with its role as a promotor of ethylene hydrogenation on Fe(100).

## 5. Summary and Conclusions

We have reported previously that ethylene adsorption on a hydrogen presaturated Fe(100) surface leads to formation of stable ethyl groups. Decomposition of the ethyl groups via $\beta$-hydride elimination at 220 K liberates gas-phase ethylene,[1] and no ethylene decomposes on the H-presaturated surface, and no ethane is formed. When CO is adsorbed onto the H-saturated surface either before or after ethylene adsorption, hydrogenation to form ethane occurs. The peak temperature of the ethane product in temperature-programmed reaction experiments is near 170 K, which is lower than the $\beta$-hydride elimination temperature of ethyl groups on the clean surface. This difference indicates that the mechanism by which CO promotes the hydrogenation of ethylene is the enhancement of the rate of the reductive elimination of ethane rather than the inhibition of the competing $\beta$-hydride elimination reaction.

When CO is adsorbed on the H-presaturated Fe(100) surface prior to adsorption of enough ethylene to saturate the surface, the ethane yield passes through a maximum of 0.14 ML of ethane at approximately 0.25 ML of CO and falls to zero at CO saturation (0.5 ML). The amount of ethylene desorbed falls to zero at CO saturation; thus high coverages of CO inhibit ethylene hydrogenation by blocking sites for ethylene adsorption. When CO is adsorbed onto the ethylene presaturated Fe(100)–H surface, the ethane yield also passes through a maximum as a function of CO coverage. Similar behavior is observed for CO adsorption onto an ethylene covered Fe(100)–H surface which has been preannealed to 175 K to form ethyl groups and desorb molecular $C_2H_4$. In these two cases displacement of adsorbed hydrocarbon species by high CO postexposures gives rise to a decrease in ethane yield at high CO coverages. The species displaced is ethylene when CO is adsorbed onto the ethylene covered surface, but ethane is displaced from the surface which has been annealed to form ethyl groups prior to CO exposure.

For H precoverage lower than saturation, threshold coverages of CO are required for ethane formation. The interdependence of the CO and H coverages at the threshold necessary to produce ethane indicates that CO must adsorb into surface regions locally concentrated with H in order for ethane formation to occur. One CO molecule is required for every four vacancies in the H adlayer in order to compress and/or restrict $H_{(a)}$ in these regions. Additional CO molecules apparently then adsorb within these H regions to induce ethane formation. Further evidence that CO must adsorb *on top* of surface regions locally concentrated with H is that the ethane yield at the same CO and H coverages is significantly higher when CO is adsorbed following $H_2$ as opposed to prior to $H_2$.

CO-induced weakening of the Fe–H bond is the most probable source of the promotion of ethyl group hydrogenation, as low-temperature $H_2$ desorption states appear when CO is adsorbed on top of an H-saturated Fe(100) surface. The population of these $H_2$ states as a function of CO coverage and their absence when $C_2H_4$ is postadsorbed to form ethane both imply that they are directly responsible for ethane formation.

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**Registry No.** $H_2C{=}CH_2$, 74-85-1; Fe, 7439-89-6; $H_3CCH_3$, 74-84-0; CO, 630-08-0.