

DATE: November 15, 1988

TITLE: Surface Properties of Iron Fischer-Tropsch Catalysts

PI's (AUTHORS): John P. Baltrus, J. Rodney Diehl, Mark A. McDonald, and Michael F. Zaroachak

INSTITUTION/ORGANIZATION: U.S. DEPARTMENT OF ENERGY, PITTSBURGH ENERGY TECHNOLOGY CENTER, P.O. BOX 10940, PITTSBURGH, PA 15236, 412-892-4570

CONTRACT NO.:

PERIOD OF PERFORMANCE: ONGOING

**OBJECTIVE:** To determine the changes in surface composition of iron oxide catalysts that occur during direct exposure to H<sub>2</sub>/CO or CO and to examine whether the activity of such catalysts can be explained based on the current knowledge of activity-structure relationships for catalysts that have been prerduced in H<sub>2</sub>.

**TECHNICAL APPROACH:** A potassium- and copper-promoted iron Fischer-Tropsch (F-T) catalyst was studied by X-ray photoelectron spectroscopy, Auger spectroscopy, and ion scattering spectrometry to determine the changes in surface speciation of iron and carbon, and the distribution of K and Cu on exposure to various pretreatment conditions. Of interest are both the effects of exposing the catalyst to H<sub>2</sub>/CO or CO and the effects of the presence of water vapor in the reaction atmosphere. The results of this work are compared to those of a previous study of the slurry-phase F-T activity of the iron catalysts in which Mössbauer spectroscopy was used to characterize the bulk composition of the catalysts.

**SIGNIFICANT ACCOMPLISHMENTS:** A transformation in surface composition from Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub> → iron carbide was found to be enhanced by pretreating catalysts with H<sub>2</sub>/CO versus CO and retarded by the addition of water vapor to the gases. A lower initial F-T activity, observed for H<sub>2</sub>/CO- versus CO-pretreated catalysts, may be explained by greater coverage of the "active" carbide species by surface carbonaceous material formed during pretreatment.

**PUBLICATIONS:** J.P. Baltrus, J.R. Diehl, M.A. McDonald, and M.F. Zaroachak, "Effects of Pretreatment of the Surface Properties of Iron Fischer-Tropsch Catalysts," Appl. Catal. submitted. Also presented at Pittsburgh-Cleveland Catalysis Society Meeting, April, 1988 and ACS National Meeting, June, 1988.

#### INTRODUCTION

The composition of iron Fischer-Tropsch (F-T) catalysts is often adjusted by the addition of both transition metal and alkali promoters in order to induce specific changes in catalyst performance for the conversion of synthesis gas to liquid hydrocarbons [1,2]. Significant changes in catalyst composition and structure can also result from pretreatment with various gases prior to exposure to synthesis conditions [3,4] (Figure 1). The activity and selectivity of iron F-T catalysts can be changed by controlling the relative formation of iron oxide and iron carbides during the

pretreatment step [5]. Therefore, it is important to investigate the changes in surface structure of iron F-T catalysts induced by different pretreatment conditions and to relate the changes to observed differences in catalytic activity and selectivity.

The surface composition of unpromoted iron F-T catalysts [6-8] and those promoted with manganese [4,9-14], copper [3,15], silver [3], and potassium [8,15,16] has been studied after preparation, activation, and exposure to F-T synthesis conditions. These studies have reported that metallic iron, which is formed on activation in  $H_2$ , is subsequently converted to one or more iron carbide phases on exposure to  $H_2/CO$ . The activity of these catalysts has been related to the intimacy of the iron and promoter phases, whose distribution is readily affected by the activation and synthesis conditions employed [3,15]. Iron-support interactions can also influence the chemical/physical properties and catalytic behavior of iron catalysts [17,18]. The chemical nature and activity of carbon and carbonaceous deposits on Fe surfaces have also been studied [19,20]. An increase in F-T activity for iron catalysts has been correlated to an increase in the ratio of carbidic to graphitic carbon on the catalyst surface [6,19]. The activity of the iron surface in secondary hydrogenation reactions affects catalyst selectivity and the relative accumulation of surface hydrocarbon species [6]; the hydrogenation activity can be lowered by the deposition of K on the iron surface [16].

Almost all of the earlier characterization and F-T activity measurements for iron catalysts have been performed after the catalysts were fully reduced in  $H_2$ . However, it is commonly accepted that the working catalyst contains a mixture of iron phases including iron oxides [5,21]. This mixture of iron phases with its associated catalytic activity can also be obtained by direct exposure of the oxide (unreduced) catalyst to  $H_2/CO$  or CO [19,22,23]. Studies of the latter catalysts are seldom reported. Some controversy arises though when one compares the results of studies of the activity and composition of prereduced and unreduced iron F-T catalysts. It has been suggested that carbon associated with iron oxides is active and iron carbide is unreactive for the formation of hydrocarbons for unreduced iron catalysts [23]. Most studies of prereduced catalysts attribute their activity to the presence of iron carbide [16,19,24]. Still another study states that both types of carbon are active for the formation of hydrocarbons [25]. Therefore it is important to determine the changes in surface composition of iron oxide catalysts that occur during direct exposure to  $H_2/CO$  or CO and to examine whether the activity of such catalysts can be explained based on the current knowledge of activity-structure relationships for catalysts that have been prereduced in  $H_2$ .

The present study is specifically intended to address the above concerns by examining the changes in surface chemical states of iron and in the distribution of the K and Cu promoters in an iron F-T catalyst on exposure to various activation treatments. Of interest are both the effects of exposing the catalyst to  $H_2/CO$  or CO and the effects of the presence of water vapor in the reaction atmosphere. The effects of added water are particularly relevant to the state of the iron catalyst under real F-T conditions, since the reducing gas of  $H_2/CO$  becomes oxidizing at moderate conversions owing to the water that is produced [24].

This work is intended to complement a separate study of the effects of catalyst pretreatment on synthesis behavior in which Mössbauer spectroscopy was used to characterize the bulk composition of catalysts removed from a slurry-phase reactor [22] (Figures 2 and 3). In this study it was found that the activity (measured as %CO conversion) of a CO-pretreated catalyst was initially slightly higher than for a catalyst given no pretreatment before exposure to reaction conditions. A decline in activity with time on stream was observed for both catalysts and was much greater for the catalyst given no pretreatment. This catalyst was initially selective to formation of C<sub>3</sub>+ hydrocarbons, but the selectivity changed towards lighter products as the catalyst deactivated. The CO-pretreated catalyst initially favored formation of light products but shifted towards heavier products as CO conversion decreased.

Mössbauer spectra of the as-prepared catalyst showed exclusively  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Following 24 hours of pretreatment in CO, the catalyst was essentially completely carbided to  $\chi$ -carbide, with traces of Fe<sub>3</sub>O<sub>4</sub> visible in the spectrum. Further reaction for up to 72 hours in syngas resulted in conversion of some iron carbide to Fe<sub>3</sub>O<sub>4</sub>. Mössbauer spectra of the catalyst treated with H<sub>2</sub>/CO for 24 hours showed mainly hexagonal  $\epsilon'$ -Fe<sub>2.2</sub>C and small amounts of  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>; further reaction eventually resulted in complete conversion to iron carbide.

#### EXPERIMENTAL

The procedure for preparation of the catalyst is outlined in Figure 4. The catalyst was prepared in a continuous precipitation unit, where a flowing aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> was mixed with another flowing solution of NH<sub>4</sub>OH. The pH of precipitation was held constant at 7.0. Each preparation yielded about 50 g of catalyst precursor after the precipitate was filtered, washed, and dried at 383 K for 48 hours in N<sub>2</sub>, then for 24 hours in vacuum. A master batch containing 65% Fe, 0.6% Cu, and oxygen as the balance (wt%) was obtained by thoroughly mixing component batches of similar composition and surface area. A 50-g sample of the master batch was impregnated (wet impregnation) with a K<sub>2</sub>CO<sub>3</sub> solution to yield a loading of 0.29% K. The sample was dried at 383 K for 24 hours and then calcined in air with the temperature raised stepwise to 623 K.

Auger electron spectra and X-ray photoelectron (XPS) spectra were collected using a Leybold-Hereaus LHS-10 instrument equipped with a stainless-steel microreaction chamber (approx. 10 cc). Catalyst samples were pressed into 0.5-mm-thick wafers and secured to a heatable-coolable rod using a Ta cover slip. The same catalyst wafer was treated sequentially for up to 24 hours; either CO (553 K) or H<sub>2</sub>/CO (1/1, 533 K) was used at a flow rate of approximately 10 cc/min and at a pressure of 101.3 kPa. In a separate set of experiments, water vapor was added to the gas streams by bubbling the gas through a water saturator containing deoxygenated deionized water. The gas lines and reaction chamber walls were heated to prevent condensation. The XPS spectra were acquired using a Leybold LHS-10 spectrometer equipped with a Mg anode (Mg K $\alpha$  = 1253.6 eV) and operated at a pass energy of 100 eV. The XPS binding energies for the calcined catalysts were referenced to the contaminant (from exposure to atmosphere) C 1s peak at 284.6 eV. Owing to changes in the chemical state of carbon for the treated catalysts, binding energies were referenced to the Cu 2p<sub>3/2</sub> peak at 932.4 eV; it was found, by

use of the Cu Auger parameter, that Cu was completely reduced to the metal in all treated catalysts. Auger analyses were performed using a 3-keV electron beam focused to an approximately 1-mm-diameter spot; the measured beam current was about 2  $\mu$ A. Spectra were collected in the N(E) mode and differentiated, typically using a modulation amplitude of 3 eV.

Ion scattering spectrometry (ISS) measurements of oxidic and H<sub>2</sub>-reduced catalysts were performed with a 3M ISS/SIMS spectrometer and data processor. The powdered samples were pressed into 13-mm pellets, and the analyses were performed at a <sup>4</sup>He pressure of  $2.7 \times 10^{-3}$  Pa. A 2-keV <sup>4</sup>He<sup>+</sup> ion beam was rastered on the sample, and the scattered ions were analyzed with a cylindrical mirror analyzer; spectra were averaged over 5-minute intervals. The surface was etched at a rate of approximately one monolayer per 15 minutes, based on separate measurements of thin-film reference samples. Hydrogen reduction of samples for ISS analysis was carried out in a tube furnace (H<sub>2</sub>, 90 cc/min, 533 K or 673 K, 1 hr); the reduced samples were transferred to the instrument without exposure to air by means of a sealable probe [26].

X-ray diffraction patterns were obtained with a Rigaku computer-controlled diffractometer equipped with a long fine-focus Cu X-ray tube, a diffracted beam graphite monochromator to provide monochromatic CuK<sub>α</sub> radiation, and a scintillation detector. When collecting data from the samples, step-scans were made at 0.1° intervals, and counting times varied from 5 to 60 seconds per step according to the intensity of the diffraction peak.

The experimental procedure and discussion for the slurry-phase F-T activity measurements, the results of which have been summarized in the introduction, are given elsewhere [22]. The experimental approach is similar to that used in a previous study [13].

## RESULTS

XPS Analyses. The Fe 2p XPS spectrum of the calcined catalyst is shown in Figure 5; the Fe 2p<sub>3/2</sub> binding energy (710.8 eV) and peak shape are identical to those of Fe<sub>2</sub>O<sub>3</sub>. The Fe 2p spectra and binding energies for the Fe compounds relevant to this study (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe metal, Fe<sub>5</sub>C<sub>2</sub>) have been reported [27,28]. Weak peaks due to Cu<sup>2+</sup> and K<sub>2</sub>CO<sub>3</sub> were observed in the XPS spectra of the Cu 2p<sub>3/2</sub> and C 1s regions, respectively.

The Fe 2p XPS spectra for the catalyst following CO exposure for up to 24 hours at 553 K are shown in Figure 6. Similar XPS results were obtained either if the same catalyst sample was exposed to CO stepwise for up to 24 hours and intermittently cooled for XPS analysis or if a fresh catalyst was treated with a single CO exposure for the given reaction time. The spectra shown in Figure 6 indicate that surface Fe<sub>2</sub>O<sub>3</sub> was converted to a mixture of Fe<sub>3</sub>O<sub>4</sub> and iron carbide (707.1 eV) during CO exposure. Although the Fe 2p<sub>3/2</sub> binding energies of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are similar, Fe<sub>2</sub>O<sub>3</sub> has a distinct satellite at approximately 8 eV higher binding energy than the main Fe 2p<sub>3/2</sub> peak [27]. The absence of this satellite at approximately 718.8 eV in Figure 6 is evidence for the conversion of most, if not all, of the Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and iron carbide. Graphitic carbon, Fe<sub>3</sub>O<sub>4</sub>, and the  $\chi$  and  $\epsilon$  phases of iron carbide were identified in the bulk by X-ray diffraction (XRD) analysis of the catalyst exposed to CO for 24 hours.

The XPS spectra of the catalyst exposed to H<sub>2</sub>/CO (1/1) for up to 24 hours at 533 K, shown in Figure 7, are consistent with the conversion of surface Fe<sub>2</sub>O<sub>3</sub> to a mixture of Fe<sub>3</sub>O<sub>4</sub> and iron carbide. It is difficult to separate the Fe-containing components of the spectra shown in Figures 6 and 7 owing to uncertainties about the shape of the inelastic background for the Fe 2p region and the similarity of binding energies for the iron oxides [4,27]. However, from a rough fit of the iron carbide and iron oxide peaks in Figures 6 and 7, one can see that the fraction of iron carbide does not increase significantly until the 24-hour reaction in CO or H<sub>2</sub>/CO. A comparison of Figures 6 and 7 shows that treating the catalyst for the same period of time in H<sub>2</sub>/CO compared to CO leads to greater formation of iron carbide. However, in neither gas is the surface of the catalyst fully carbided after 24 hours. Although the Cu 2p signal was very weak after the catalysts were pretreated, it was determined that Cu<sup>2+</sup> had been completely reduced to metallic Cu for all reaction times in CO or H<sub>2</sub>/CO.

The surfaces of iron oxide catalysts can be fully carbided after short exposures to H<sub>2</sub>/CO if the oxides are reduced first in H<sub>2</sub> [6,7,16]. This behavior was also examined in the current study. Figure 8, the Fe 2p XPS spectrum of the catalyst following reduction in H<sub>2</sub> for 6 hours at 673 K, shows that surface Fe<sub>2</sub>O<sub>3</sub> was completely reduced to metallic iron. Subsequently, the catalyst was treated with either H<sub>2</sub>/CO (1/1, 533 K, 4 hr) or CO (553 K, 4 hr); the resulting Fe 2p spectra also are shown in Figure 8. Previous studies reported that carbiding of iron metal results in an approximate increase of 0.3 eV in the Fe 2p<sub>3/2</sub> binding energy [6,7,16]. The data reported here are consistent with this observation for catalysts treated in either H<sub>2</sub>/CO or CO. However, since the shift in the Fe 2p<sub>3/2</sub> binding energy is very small, it is not certain that all of the metallic iron on the surface was carbided. Analyses of the reduced catalysts following CO or H<sub>2</sub>/CO exposure by XRD showed almost exclusively the presence of iron metal and iron carbide; a fraction of the iron metal may be on the surface of the catalyst. As shown in Figure 8, the presence of a component at 710.7 eV (iron oxides) in the Fe 2p<sub>3/2</sub> spectrum of the catalyst treated with CO is evidence that this catalyst is less fully carbided than the catalyst treated with H<sub>2</sub>/CO; XRD analyses showed a trace of Fe<sub>3</sub>O<sub>4</sub> in the treated catalyst.

Changes in the surface concentration of K, relative to Fe, as a function of reaction time in CO or H<sub>2</sub>/CO can be compared in Figure 9. An increase in the K/Fe atomic ratio is observed with reaction time in CO/H<sub>2</sub>. Treatment of the catalyst with CO initially results in an increase in the K/Fe atomic ratio, but little additional change is observed until the reaction time reaches 24 hours. The K/Fe atomic ratios were greater for catalysts treated with H<sub>2</sub>/CO compared to CO for reaction times of 12 hours or longer. Prereduction of the catalysts in H<sub>2</sub> led to a significantly enhanced K/Fe atomic ratio following exposure to H<sub>2</sub>/CO when compared to unreduced catalysts reacted for 6 hours; no such enhancement was observed for the CO-treated catalysts.

Auger Analyses. Auger electron spectroscopy has been used to monitor the chemical environment of carbon, especially the formation of carbides and graphitic carbon [19,20,29-31]. The carbon KLL Auger spectra for catalysts treated with CO and H<sub>2</sub>/CO are presented in Figures 10 and 11, respectively. Typical Auger spectra for graphite and iron carbide also are shown in Figure 10. The most intense Auger transition for carbon is at approximately

272 eV; iron carbide has equally intense peaks at 272 eV and 278 eV. The shape of less intense peaks at lower kinetic energy is influenced by the chemical bonding of carbon, which affects the transition probabilities of electrons in subshells involved in the KLL transition [29]. An interference in some of the spectra at about 252 eV, owing to the LMM transition for potassium, makes the identification of the carbidic phase difficult, especially if a mixed graphite-carbide phase is present.

The spectra shown in Figure 10 for the CO-treated catalyst are composed of a carbon spectrum characteristic of graphitic carbon (peak at approximately 242 eV) and a weak potassium peak (252 eV); the contribution of the graphitic component becomes slightly greater at longer reaction times. The only discrete evidence for carbidic carbon is the small peak or shoulder on the high-energy side of the main C Auger peak. The weaker, low-energy peaks owing to carbidic carbon can be obscured if a large fraction of carbon is in the graphitic form [31]. The C Auger spectra for the H<sub>2</sub>/CO treated catalysts, shown in Figure 11, are also primarily composed of graphitic carbon and potassium peaks but may contain a small carbidic component for both the 1- and 6-hour reactions. In contrast to the spectra for the CO-treated catalysts, the C Auger spectra for catalysts treated in CO/H<sub>2</sub> for 12 and 24 hours contain no peaks other than the main carbon peak at 272 eV. The lack of peaks at lower kinetic energy may be characteristic of carbon that is in the form of long-chain alkanes, alkenes, or other hydrogenated species on the catalyst surface [29,32]. To provide additional evidence for this latter hypothesis a nickel foil, which had been sputtered clean with Ar<sup>+</sup> was analyzed with Auger after its surface was lightly dusted (to minimize charging) with crystallites of C<sub>24</sub>H<sub>74</sub>; the resulting spectrum is shown in Figure 11. Some decomposition of the alkane to graphite was observed for longer analysis times (1 hour); decomposition of carbidic carbon is not expected under similar conditions. The dominance of hydrocarbon species on the catalyst surface at longer reaction times may conceal the presence of any graphitic or carbidic species.

ISS Analyses. Peaks due to K, Cu, and Fe were not observed in the ISS spectra of catalysts exposed to CO or H<sub>2</sub>/CO for 1 hour. This was attributed to the immediate buildup of a carbonaceous layer on the catalyst surface. The catalysts were analyzed by ISS following reduction in H<sub>2</sub> at 533 K and 673 K for 1 hour; the results are presented in Table 1. The surface concentration of K relative to Fe increased upon reduction; the increase was more pronounced at the higher reduction temperature. Sputtering during the ISS analyses revealed that the increase in surface concentration of K on reduction is greatest within the first few angstroms. The concentration of Cu increased just below the first few angstroms of the surface following reduction at 533 K, as evidenced by the more gradual decrease in the Cu/Fe intensity ratio with sputtering time compared to the unreduced catalyst; no Cu signal was observed after the catalyst was reduced at 673 K.

#### Water Exposure

The Fe 2p NPS spectra of catalysts treated at 553 K for 1 and 24 hours with CO containing approximately 3.6% water vapor are shown in Figure 12; the Fe 2p spectra for catalysts treated with H<sub>2</sub>/CO (1/1) at 533 K and with 3.6% water vapor were nearly identical to those in Figure 12. The Fe 2p spectrum after the 1-hour reaction is characteristic of Fe<sub>2</sub>O<sub>3</sub>. Following

reaction for 24 hours, the satellite peak at about 718.8 eV, attributed to  $\text{Fe}_2\text{O}_3$ , is nearly absent. This observation suggests that most of the  $\text{Fe}_2\text{O}_3$  has been converted to  $\text{Fe}_3\text{O}_4$ ; XRD results supported this hypothesis. A contribution to the Fe 2p spectra by a surface iron hydroxide phase cannot be ruled out. There was no evidence in the Fe 2p spectra for the formation of iron carbide on the surface of any catalyst, in contrast to results obtained in the absence of water vapor; XRD also showed no iron carbide was present.

The addition of water vapor to the gas streams results in lower surface K/Fe atomic ratios (Table 2). Catalysts treated with  $\text{H}_2/\text{CO}$  show a more pronounced decrease in K/Fe atomic ratios in the presence of water vapor than do catalysts treated with CO. An increase in K/Fe atomic ratios is still observed with reaction time for either gas composition.

Auger analyses of the C KLL transition for catalysts treated with either CO or  $\text{H}_2/\text{CO}$  containing water vapor showed peaks characteristic of a graphitic or a mixed graphitic-hydrocarbon surface. There was no evidence for the presence of carbidic carbon on any catalysts. The primary difference between the Auger spectra of catalysts treated with CO or  $\text{H}_2/\text{CO}$  was that the C/K intensity ratio was lower for catalysts treated with CO.

## DISCUSSION

Previous studies have demonstrated correlations between the increasing activity of iron catalysts and the presence of either  $\text{Fe}_3\text{O}_4$  [23] or iron carbide [6,33]. The discrepancy concerning the nature of the active phase has arisen during studies in which the catalysts were pretreated with  $\text{H}_2$  or simply exposed to  $\text{H}_2/\text{CO}$  without prereduction. Therefore, the nature of the catalyst's pretreatment, which has a direct effect on the surface and bulk composition, can affect its subsequent activity. The surface of a catalyst treated in the XPS reaction chamber is probably not identical to that of a catalyst during reaction in a stirred autoclave. However, relative changes in the surface composition of iron catalysts that occur on exposure to different pretreatment gases in the XPS reaction chamber can form the basis for predicting the types of changes that might occur on the surfaces of catalysts exposed to similar gas compositions in a slurry-phase reactor.

The varying effects of catalyst pretreatment on surface composition are clearly demonstrated by the results reported here; the surface and bulk compositions may not be identical. The XPS results shown in Figure 8 are consistent with earlier studies [6,7,16] reporting the complete reduction of iron oxide to metallic iron in  $\text{H}_2$  and its subsequent ease of conversion to iron carbide in  $\text{H}_2/\text{CO}$ . These results are also consistent with previous reports that carbiding is more extensive in  $\text{H}_2/\text{CO}$  than in CO [34]. The catalyst treated with CO after reduction in  $\text{H}_2$  did show partial oxidation of surface iron to  $\text{Fe}_3\text{O}_4$ , while the  $\text{H}_2/\text{CO}$ -treated sample showed no surface oxide. Such behavior may be attributed to the dissociation of CO on the iron surface and the absence of  $\text{H}_2$  in the pretreatment gas. The dissociation of CO on Fe surfaces can lead to the formation of surface iron carbide and iron oxides, which can subsequently be reduced in the presence of  $\text{H}_2$  [5]:





The iron surface also can be regenerated by CO:



Therefore, the observation of a surface iron oxide phase following reaction in CO, as opposed to H<sub>2</sub>/CO, may indicate that reaction 2 proceeds faster than reaction 3 on the iron surface. Formation of Fe<sub>3</sub>O<sub>4</sub> on the surface of Fe metal following reaction in CO at 473 K has recently been observed using Raman spectroscopy [25]. Oxidation by CO<sub>2</sub> and H<sub>2</sub>O in the reverse of reactions 6 and 7, respectively, is unlikely to play a major role because of their small partial pressures at low conversion in the differential reactor.

The mechanism for the reaction of metallic iron with CO and H<sub>2</sub>/CO also may be used to explain the behavior observed when the as-prepared catalyst is treated with CO or H<sub>2</sub>/CO. A comparison of Figures 6 and 7 shows that H<sub>2</sub>/CO is more conducive to the formation of iron carbide than is CO. This may be due to more rapid removal of surface oxygen with H<sub>2</sub> than with CO, as has been postulated for catalysts that are initially metallic [34]. The fact that the surface iron is not totally carbided after 24 hours of reaction in CO or H<sub>2</sub>/CO is consistent with the results of previous studies in which Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> was reacted without prereduction [23,25]. Longer reactions (greater than 24 hours) in H<sub>2</sub>/CO may eventually lead to complete conversion of surface iron to iron carbide, as Mössbauer experiments have demonstrated for the case of bulk iron carbide formation [22].

The partial pressure of water vapor resulting from high syngas conversions also impedes the transformation of Fe<sub>3</sub>O<sub>4</sub> to iron carbide. This is supported by the results from the second set of experiments, which show that the addition of water to the syngas mixture considerably slows the conversion process: Fe<sub>2</sub>O<sub>3</sub> + Fe<sub>3</sub>O<sub>4</sub> + iron carbide. The inhibition of iron carbide formation by water vapor in CO-treated catalysts is seen by comparing the XPS spectra in Figures 6 and 12. Water may also help to oxidize some iron carbide back to Fe<sub>3</sub>O<sub>4</sub>, as demonstrated by the Mössbauer results [22]. The presence of water in the atmosphere surrounding the catalysts can affect their surface composition and may alter their long-term catalytic reactivity. Therefore, the production of water, which occurs when treating a catalyst with H<sub>2</sub>/CO (Equations 1 and 2) or during exposure to syngas following pretreatment in CO, can be partially responsible for the observed decrease in catalytic activity with time on stream at higher conversions in the slurry-phase reactor [22]. It is important to remember that the effects of water can be more dramatic at the surface than in the bulk.

The presence of water vapor in the gas streams is only one of several variables that can affect the F-T activity of iron catalysts. Other important variables are the chemical forms of carbon and the degree to which it covers the surface of the catalyst [7,16,19,23]. The three major types of carbon commonly found in CO- or H<sub>2</sub>/CO-treated iron catalysts are iron carbide, graphitic carbon, and hydrocarbon species formed by the F-T reaction. The formation of large deposits of carbonaceous material on the catalyst surface is supported by the fact that the principal components of the catalyst are obscured from ion scattering following pretreatment.



The Auger data presented in Figures 10 and 11 show that graphitic carbon is a large fraction of the surface carbon on the pretreated catalysts. Graphitic carbon is often referred to as "inactive" carbon [19] in the F-T reaction, while carbidic carbon is considered "active" [16,19,24]. Although the relative proportions of graphitic and carbidic carbon may be different on a given catalyst in a slurry-phase reactor as opposed to the XPS reactor, it can still be realistic to compare the relative proportions of carbon species formed for the same catalyst under the two different pretreatment atmospheres. A comparison of Figures 10 and 11 shows that after 24 hours, the CO-treated catalyst has a slightly greater proportion of carbidic surface carbon than the CO/H<sub>2</sub> treated catalyst, for which "hydrocarbon-like" carbon is the dominant surface species. This finding can tentatively be explained if one assumes that the initial activity and selectivity differences of these catalysts in the XPS reaction chamber are qualitatively similar to those observed in the slurry-phase reactor [22]. The higher F-T activity of CO-pretreated catalysts in the slurry-phase reactor is consistent with the finding that catalysts pretreated with CO in the XPS reaction chamber have a greater fraction of "active" carbidic carbon on the surface compared to catalysts pretreated with H<sub>2</sub>/CO. Also, the catalysts pretreated with CO/H<sub>2</sub> initially produced heavier products in the slurry-phase reactor, which may explain why a large fraction of hydrocarbon-like carbon is found on the surface of the catalyst pretreated with CO/H<sub>2</sub> in the XPS reaction chamber. Differences in the types of iron carbide may also affect catalyst activity and selectivity.

An increase in hydrocarbon species on the surface of the catalysts, especially those exposed to H<sub>2</sub>/CO, at longer pretreatment times may be correlated to an increase in the fraction of K on the surface (Figure 9), since K promotes hydrocarbon growth [16]. Migration of K to the surface of Fe catalysts in a H<sub>2</sub>/CO atmosphere has been observed previously [15]. The migration of K can be attributed to the reducing nature of the pretreatment gas based on previous studies [35] and the data reported in Figure 9 and Tables 1 and 2. The behavior of K and Cu may also modify the activity/selectivity of the iron catalysts and play a role in determining the observed differences in the behavior of CO/H<sub>2</sub>- and CO-pretreated catalysts.

The behavior and effects of the Cu promoter during pretreatment are not clear (other than being fully reduced) owing to its low concentration. The ISS results (Table 1) show that the surface concentration of Cu is diminished under strictly reducing conditions. This can be due to sintering of the Cu phase [3], coverage of Cu by the K that has migrated to the surface, or formation of a mixed Fe-Cu phase.

It is apparent from the results of this study that the chemical state of iron in K- and Cu-promoted Fe F-T catalysts is dependent upon the catalyst pretreatment conditions. Formation of an "active" surface iron carbide is favored by pretreatment in H<sub>2</sub>/CO versus CO. However, the ultimate activity of the catalyst is governed by the degree to which iron carbide is exposed on the catalyst surface as opposed to being covered by inactive carbonaceous material. This study further indicates that the deposition of inactive carbonaceous material on the catalyst's surface from pretreatment in H<sub>2</sub>/CO is greater than that from pretreatment in CO. The nature of such carbonaceous material is affected by the amount of K on the catalyst's surface, which is influenced by the type of pretreatment.

#### ACKNOWLEDGMENTS

The authors thank S.S. Pollack for providing supporting XRD data and J.R. D'Este for contributions to the ISS study. Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

#### REFERENCES

- 1 H.H. Storch, N. Columbic, and R.E. Anderson, "The Fischer-Tropsch and Related Synthesis," John Wiley & Sons, New York, N.Y., 1951.
- 2 H. Koelbel and M. Ralek, *Cat. Rev.-Sci. Eng.*, 21 (1980) 225.
- 3 I.E. Wachs, D.J. Dwyer, and E. Iglesia, *Appl. Catal.*, 12 (1984) 201.
- 4 T. Grzybek, H. Papp, and M. Baerns, *Appl. Catal.*, 29 (1987) 335.
- 5 D.J. Dwyer and G.A. Somorjai, *J. Catal.*, 52 (1978) 291.
- 6 D.J. Dwyer and J.H. Hardenbergh, *J. Catal.*, 87 (1984) 66.
- 7 C.S. Kuivila, P.C. Stair, and J.B. Butt, *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, 31 (1986) 218.
- 8 D.J. Dwyer and J.H. Hardenbergh, *Prepr.-Am. Chem. Soc., Div. Pet. Chem.*, 29 (1984) 715.
- 9 K.B. Jensen and F.E. Massoth, *J. Catal.*, 92 (1985) 98.
- 10 K.B. Jensen and F.E. Massoth, *J. Catal.*, 92 (1985) 109.
- 11 T. Grzybek, H. Papp, and M. Baerns, *Appl. Catal.*, 29 (1987) 351.
- 12 I.S.C. Hughes and J.O.H. Newman, *Appl. Catal.*, 30 (1987) 303.
- 13 J.M. Stencel, J.R. Diehl, S.R. Miller, R.A. Anderson, M.F. Zaroachak, and H.W. Pennline, *Appl. Catal.*, 33 (1987) 129.
- 14 U. Lindner and H. Papp, *Appl. Surf. Sci.*, 32 (1988) 75.
- 15 E.J. Karwacki, Jr., *Microbeam Anal.*, 21 (1986) 609.
- 16 D.J. Dwyer and J.H. Hardenbergh, *Appl. Surf. Sci.*, 19 (1984) 14.
- 17 J.L. Rankin and C.H. Bartholomew, *J. Catal.*, 100 (1986) 526.
- 18 J.L. Rankin and C.H. Bartholomew, *J. Catal.*, 100 (1986) 533.
- 19 H.J. Krebs and H.P. Bonzel, *Surf. Sci.*, 88 (1979) 269.
- 20 H.P. Bonzel and H.J. Krebs, *Surf. Sci.*, 91 (1980) 499.

- 21 W.M. Shen, J.A. Dumesic, and C.G. Hill, *Rev. Sci. Instrum.*, 52 (1981) 858.
- 22 M.A. McDonald and M.F. Zarochak, in preparation.
- 23 J.P. Reymond, P. Meriaudeau, and S.J. Teichner, *J. Catal.*, 75 (1982) 39.
- 24 P. Biloen and W.M.H. Sachtler, *Advan. Catal.*, 30 (1981) 165.
- 25 M. Watanabe and T. Kadowaki, *Appl. Surf. Sci.*, 28 (1987) 147.
- 26 K.T. Ng and D.M. Hercules, *J. Phys. Chem.*, 80 (1976) 2094.
- 27 D.D. Hawn and B.M. Dekoven, *Surf. Int. Anal.*, 10 (1987) 63.
- 28 C.S. Kuivila, J.B. Butt, and P.C. Stair, *Appl. Surf. Sci.*, 32 (1988) 99.
- 29 B. Lesiak, P. Mrozek, A. Jablonski, and A. Jozwick, *Surf. Int. Anal.*, 8 (1986) 121.
- 30 H.H. Madden, *J. Vac.Sci. Technol.*, 18 (1981) 677.
- 31 M.A. Smith, S. Sinharoy, and L.L. Levenson, *J. Vac. Sci. Technol.*, 16 (1979) 462.
- 33 R.R. Rye, D.R. Jennison, and J.E. Houston, *J. Chem. Phys.*, 73 (1980) 4867.
- 33 G.B. Raupp and W.N. Delgass, *J. Catal.*, 58 (1979) 361.
- 34 E.E. Unmuth, L.H. Schwartz, and J.B. Butt, *J. Catal.*, 63 (1980) 404.
- 35 G. Connell and J.A. Dumesic, *J. Catal.*, 92 (1985) 17.

Table 1. ISS Intensity Ratios for K- and Cu-Promoted Fe Catalysts.

Sputtering Time (min)	K/Fe				Cu/Fe			
	0-5	5-10	15-20	55-60	0-5	5-10	15-20	55-60
As Prepared	0.81	0.20	0.10	0.03	1.22	0.78	0.69	0.64
533 K, 1 hr, H <sub>2</sub>	3.00	0.26	0.12	0.06	1.00	0.93	0.93	0.92
673 K, 1 hr, H <sub>2</sub>	13.3	7.2	1.3	0.67	0	0	0	0

Table 2. K/Fe Atomic Ratios for K- and Cu-Promoted Fe Catalysts.

	Treated with CO, 553 K		Treated with H <sub>2</sub> /CO (1/1), 533 K	
	No H <sub>2</sub> O	With H <sub>2</sub> O	No H <sub>2</sub> O	With H <sub>2</sub> O
As Prepared (Not Treated)	0.07	-----	0.07	-----
Treated 1 hr	0.70	0.31	0.36	0.13
Treated 6 hr	0.65	0.43	0.63	0.16
Treated 12 hr	0.68	0.41	2.91	0.23
Treated 24 hr	0.82	0.68	4.24	0.25
Pretreated H <sub>2</sub> , 673 K, 4 hr, then treated 4 hr	0.75	-----	14.0	-----

Note: Ratios were calculated from XPS K 1s/Fe 2p intensity ratios using sensitivity factors provided by the instrument manufacturer; the intensity ratios were measured with a precision of  $\pm 10\%$  (rsd) or better.

## PRETREATMENT EFFECTS ON Fe CATALYSTS

- Purpose of pretreatment clear for most F-T catalysts
  - Ru, Co, Ni reduced in H<sub>2</sub>
  - Catalysts stay reduced during synthesis
- Purpose of Fe catalyst pretreatment unclear
  - Active catalyst can contain  $\alpha$ -Fe, Fe oxide, Fe carbide(s)
  - Reduction in H<sub>2</sub> one of many pretreatments
  - Pretreated catalyst changes composition during synthesis
- Fe pretreatment very empirical
- **This work** — Effects of two pretreatments and exposure to H<sub>2</sub>O
  - (a) "Induction" at synthesis conditions (533 K, 1/1 H<sub>2</sub>/CO)
  - (b) CO-pretreatment (553 K)
  - (c) (a) or (b) plus 3.6% H<sub>2</sub>O vaporX-ray photoelectron spectroscopy, Auger spectroscopy, Ion scattering spectrometry, X-ray diffraction



## SLURRY PHASE F-T SYNTHESIS WITH PRECIPITATED IRON CATALYSTS

- Catalyst prepared in continuous precipitation unit
  - Solution of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$  continuously flows into stirred unit
  - Continuous flow of  $\text{NH}_4\text{OH}$  solution gives precipitate
  - Samples filtered and washed, oven-dried
- Impregnation with  $\text{K}_2\text{CO}_3$  solution
  - Impregnated to wetness
  - Samples oven-dried
  - Calcination in air, final temperature 623 K
- Compositions —

%Fe	65
Cu	0.6
K	0.29

Figure 4. Catalyst Preparation Procedure

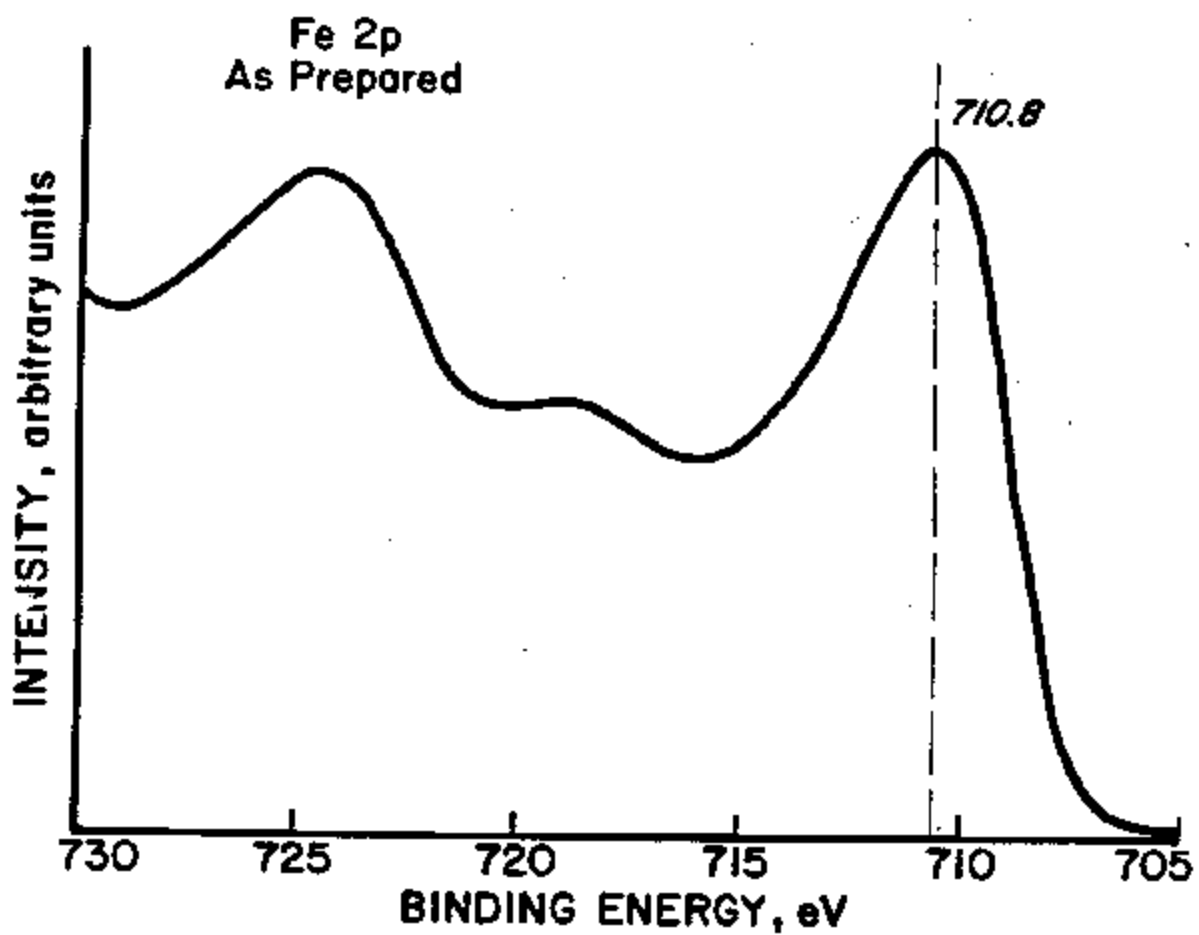


Figure 5. The XPS Fe 2p Spectrum of the As-Prepared K/Cu-Fe Catalyst.



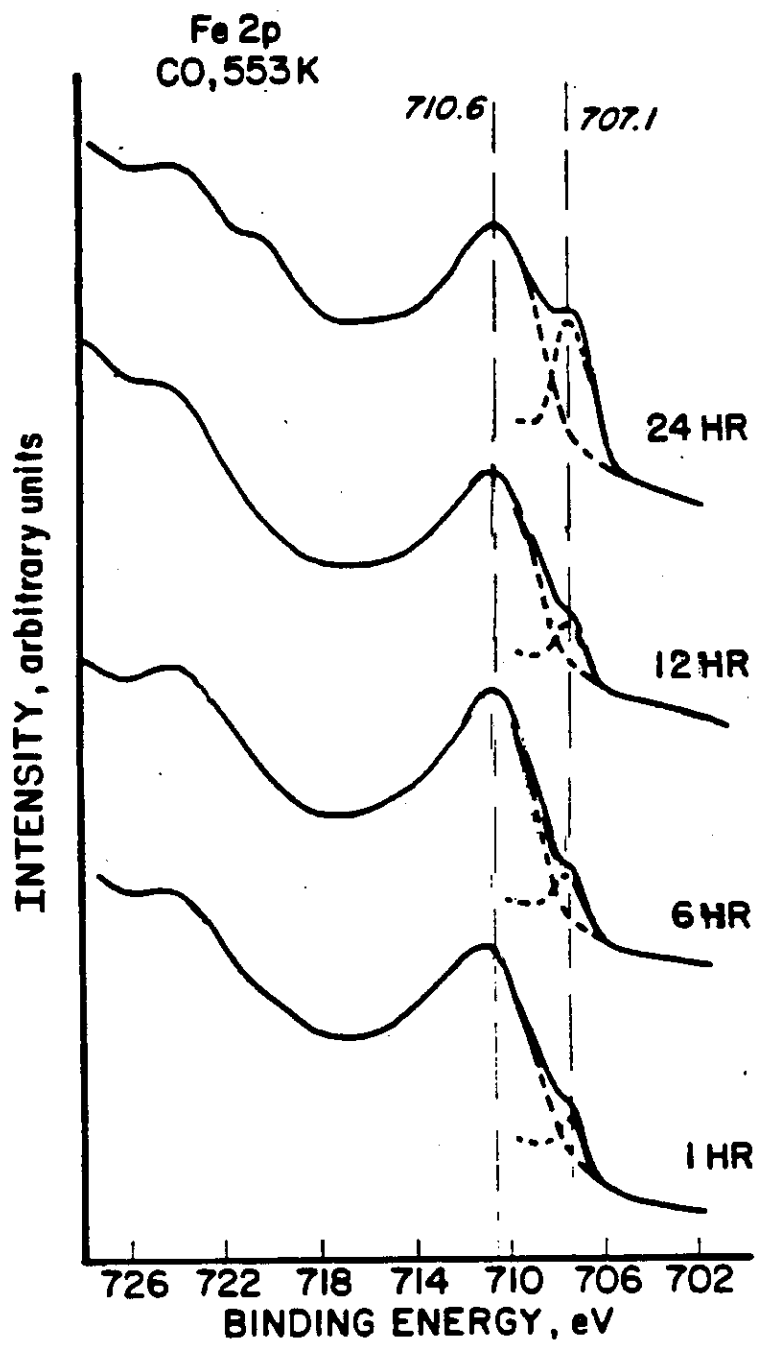


Figure 6. The XPS Fe 2p Spectra of K/Cu-Fe Catalyst Treated with CO (553 K, 1-24 hr).

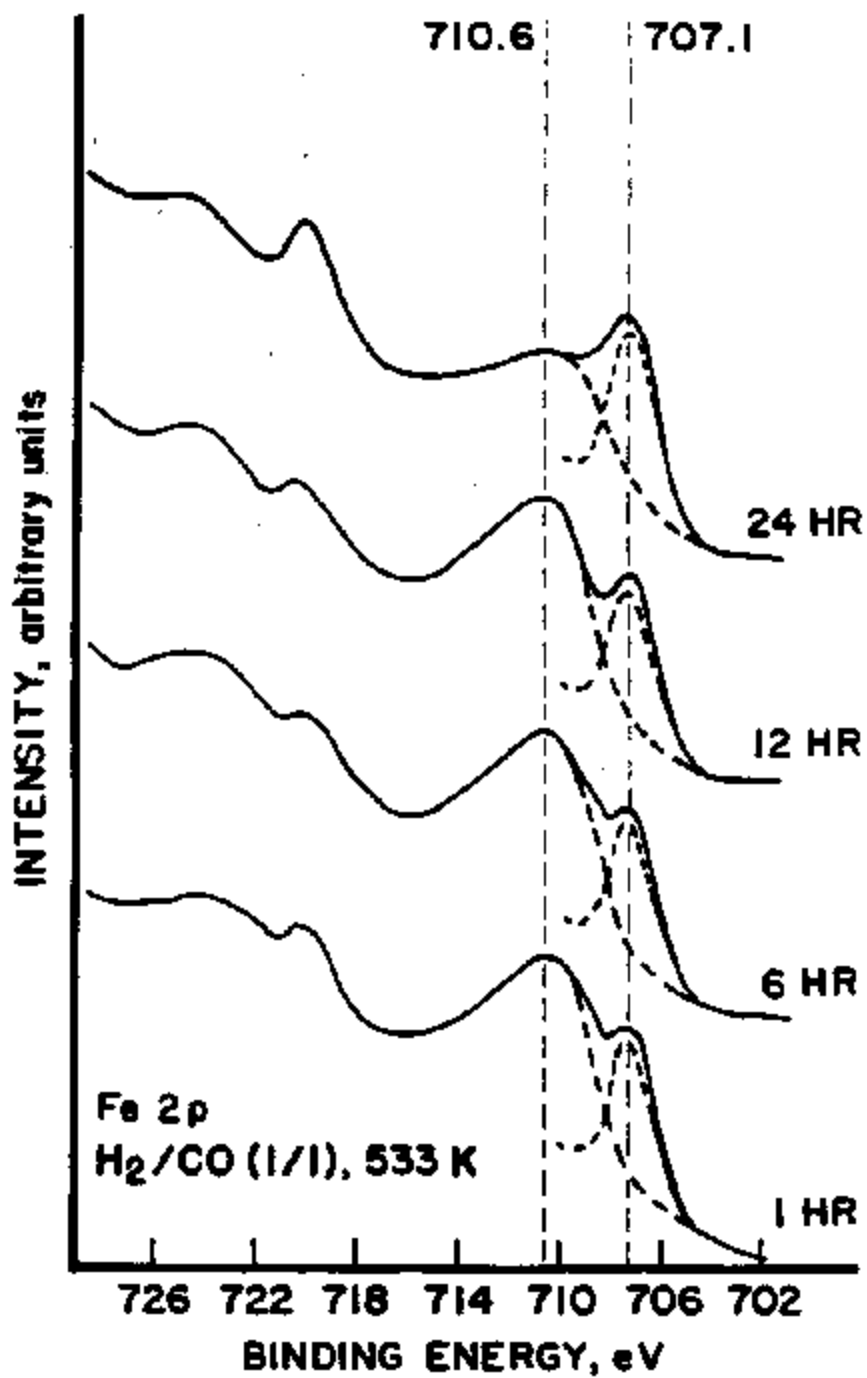


Figure 7. The XPS Fe 2p Spectra of K/Cu-Fe Catalyst Treated with  $H_2/CO$  (1/1, 533 K, 1-24 hr).

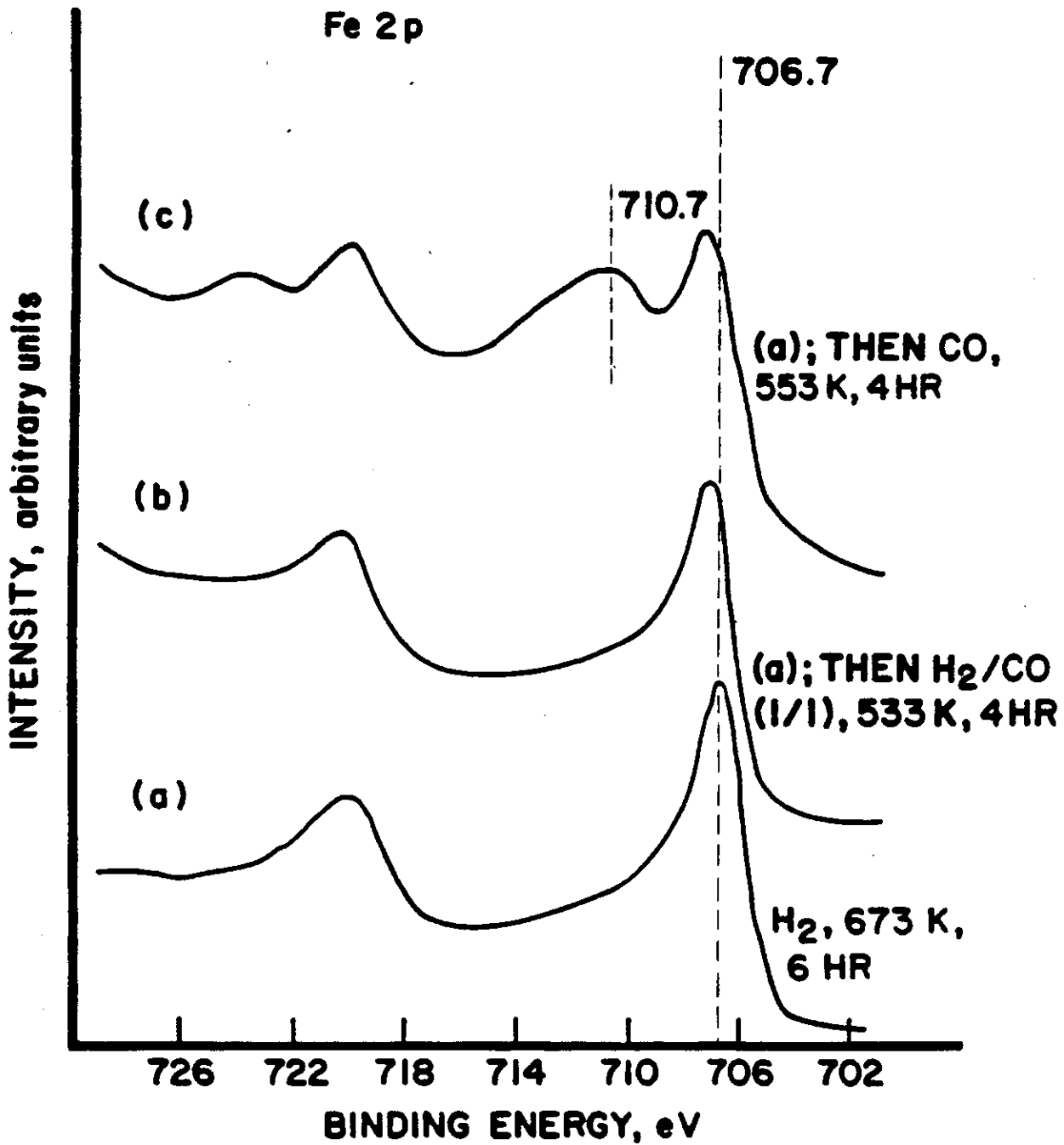


Figure 8. The XPS Fe 2p Spectra of K/Cu-Fe Catalysts After Reduction and Followed by CO or H<sub>2</sub>/CO Treatments.

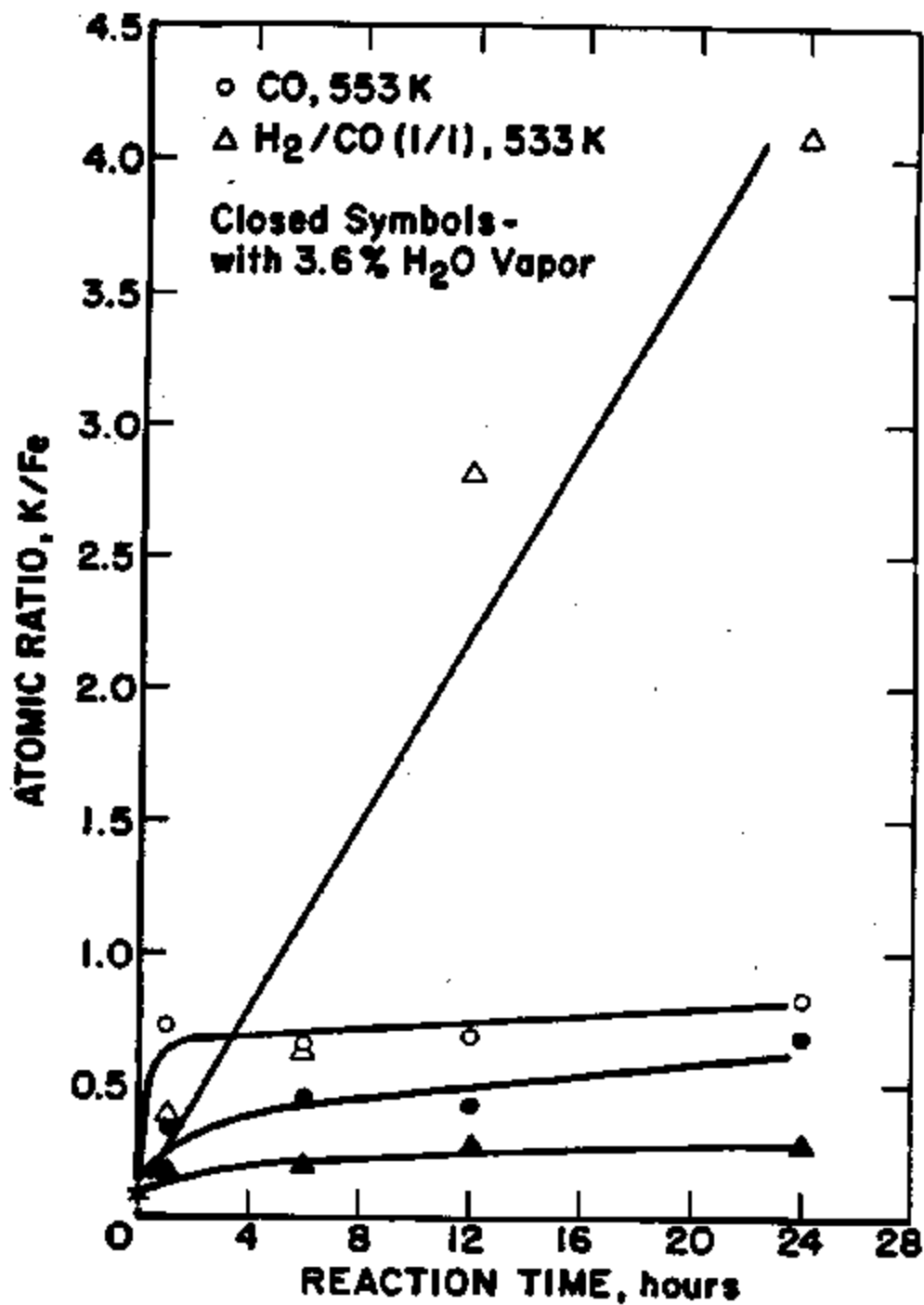


Figure 9. The XPS K/Fe Atomic Ratios for K/Cu-Fe Catalyst Treated with CO (553 K, 1-24 hr) or H<sub>2</sub>/CO (1/1, 533 K, 1-24 hr).

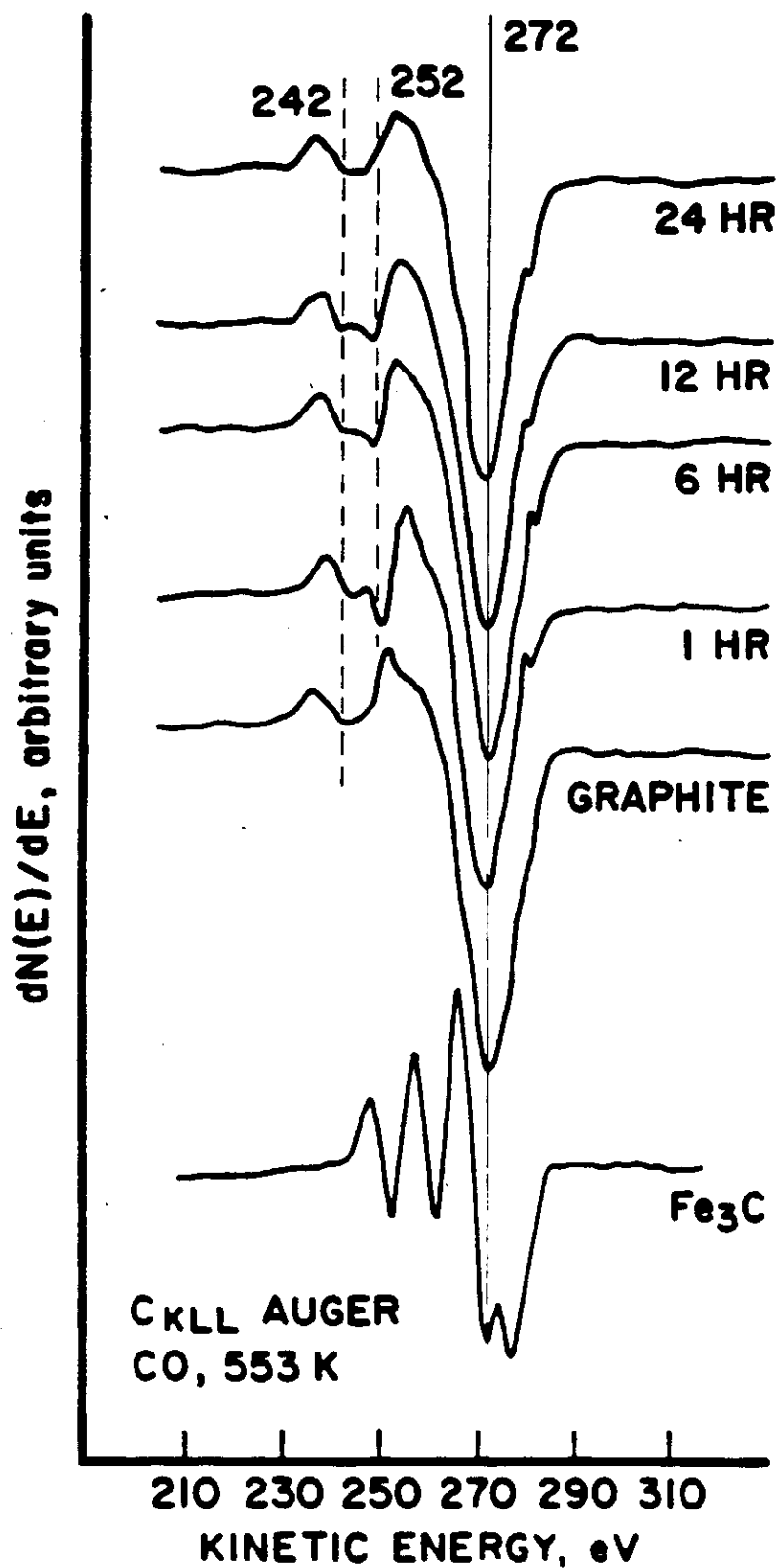


Figure 10. Carbon KLL Auger Spectra of K/Cu-Fe Catalyst Treated With CO (553 K, 1-24 hr); and the Reference Compounds: Graphite and  $\text{Fe}_3\text{C}$  [ $\text{Fe}_3\text{C}$  spectrum from K. Hirokawa et al., J. Elect. Spect. Relat. Phenom., 35 (1985) 319. Reproduced with permission.].

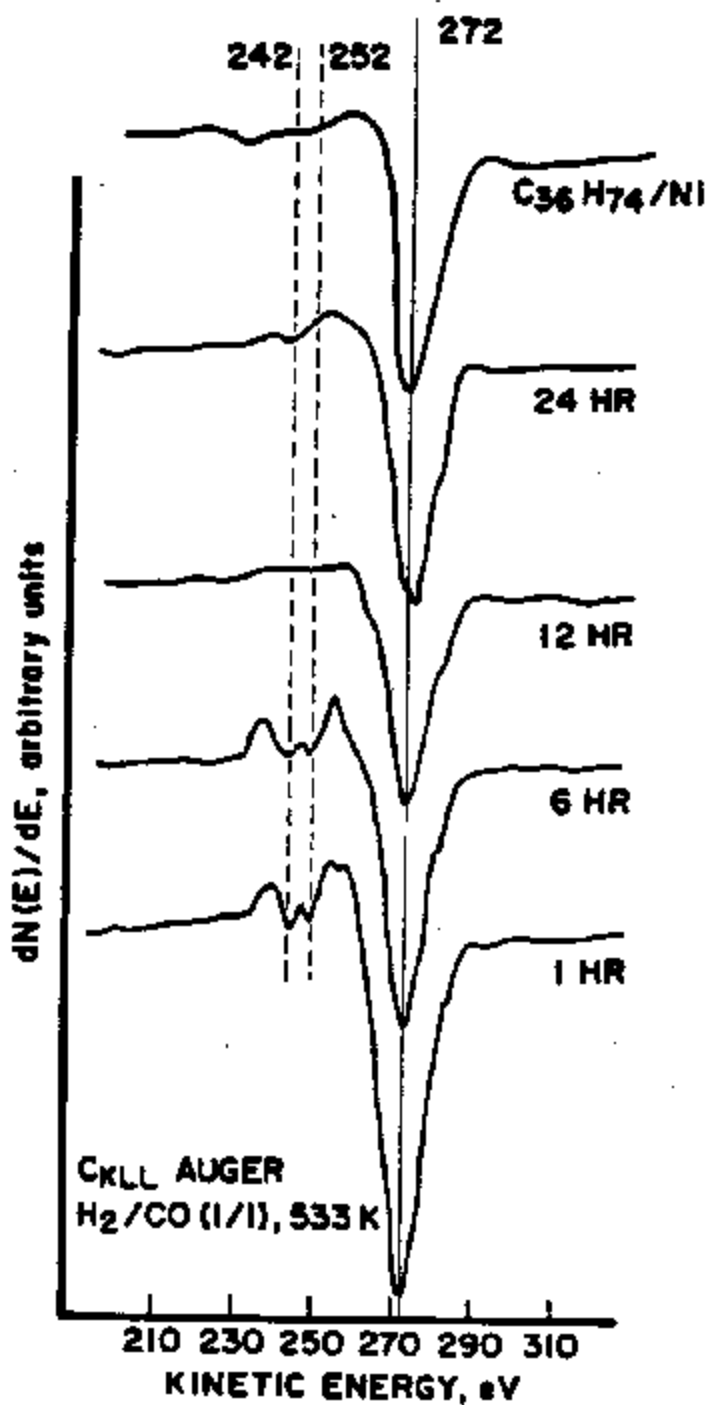


Figure 11. Carbon KLL Auger Spectra of C<sub>36</sub>H<sub>74</sub> on Ni Foil; and the K/Cu-Fe Catalyst Treated With H<sub>2</sub>/CO (1/1, 533K, 1<sup>36</sup>/<sub>24</sub> Hr).

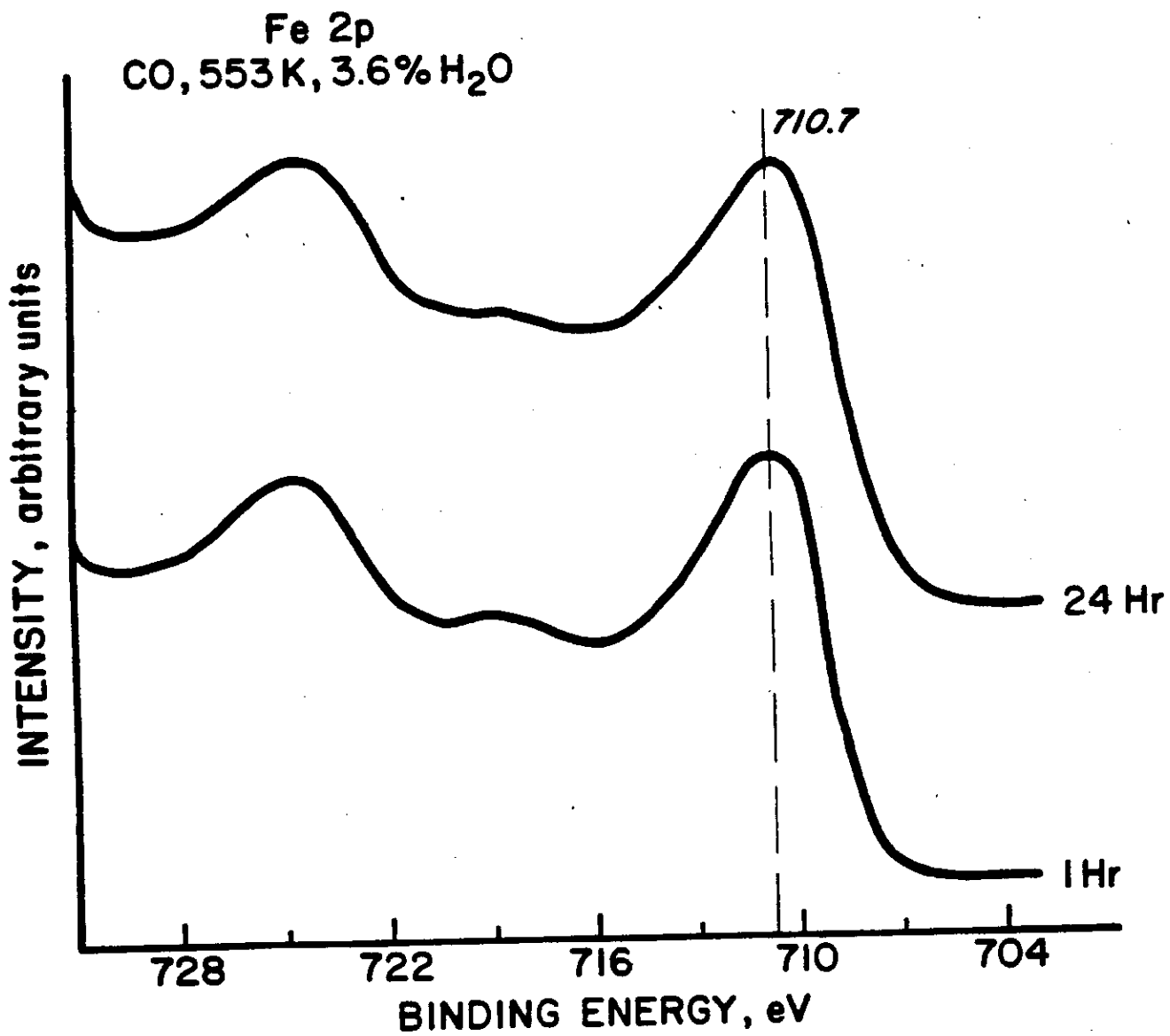


Figure 12. The XPS Fe 2p Spectra of K/Cu-Fe Catalysts Treated With CO Containing 3.6% Water Vapor (553 K, 1-24 hr).