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An *in Situ* Infrared Study of CO Hydrogenation over Silica and Alumina-Supported Ruthenium and Silica-Supported Iron

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The synthesis of hydrocarbons from carbon monoxide and hydrogen over Ru/SiO_2, Ru/Al_2O_3, and Fe/SiO_2 catalysts has been studied under reaction conditions by infrared spectroscopy. Other than CO, the surface species which are observed during reaction contain only carbon and hydrogen. Strong CH_2 bands arising from long chain saturated hydrocarbons are observed at low reaction temperatures ($T < 473$ K) with ruthenium but not with iron. With increasing temperature, these CH_2 bands on Ru decrease and are replaced by a single broad band. This may be a composite of CH_2 and CH_3 groups having one or at most a few carbon units attached to the metal surface. At these higher temperatures the spectra from Ru/SiO_2 and Fe/SiO_2 catalysts become similar, suggesting common surface intermediates. Additionally, at these temperatures bands corresponding to gas phase products (methane, ethane, propane) are also observed. Differences in the temperature dependence of the hydrocarbon bands from Ru/SiO_2 and Fe/SiO_2 are shown to be consistent with other published results. No evidence is found for the existence of hydroxy carbene or formyl species during reaction, adding to growing evidence that hydrocarbon synthesis over ruthenium and iron proceeds via initial formation of surface carbides.

INTRODUCTION

Studies aimed at characterizing the catalytic surface can perhaps be categorized as belonging to two types, static and dynamic. The former are more prevalent, and include spectroscopic studies using probe molecules on surfaces as well as many of the new techniques which require ultrahigh vacuum. While these provide useful information on fresh or used catalyst surfaces and their interaction with adsorbates, a question which must be addressed is whether the prevalent species or prevalent sites observed under static conditions are the ones of importance when the actual catalytic reaction is taking place. Subjecting the catalyst to reaction (dynamic) conditions while simultaneously monitoring the surface offers the possibility of determining the species or sites which are truly important in the synthesis.

Infrared spectroscopy is one of the more readily applicable techniques for such dynamic studies. This may be especially true for CO + H_2 reactions, since CO is a reactant as well as a common infrared spectroscopic probe molecule. The Fischer–Tropsch catalyst surface has been studied during reaction by Blyholder and Neff (iron/silica) (*1*), Dalla Betta and Shelef (ruthenium/alumina) (*2*), and Ekerdt and Bell (ruthenium/silica) (*3*). Blyholder and Neff observed bands in the CH and OH regions and postulated that alcoholic species were present on the surface during reaction. This tended to corroborate a long hypothesized "enolic" intermediate. Dalla Betta and Shelef suggested that the CH and OH groups of these "alcoholic" species were simply hydrocarbons and water adsorbed on the support. They saw no evidence of any active species other than CO being attached to the ruthenium, although they did observe hydrocarbon bands, which were attributed to products adsorbed on the alumina. These bands (2928, 2850 cm^{-1}), however, were somewhat different from the single broad band observed by Blyholder

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and Neff (2940 cm^{-1}). Ekerdt and Bell saw CO as the major observable component on the catalyst surface, although hydrocarbon bands were also observed which they felt were bound to ruthenium rather than to the silica support.

All three works hint at some of the drawbacks of dynamic studies which should be emphasized:

(1) Reaction products may tend to obscure the catalytic event, especially if they are adsorbed strongly by the support.

(2) Reactions may occur and species may be formed on the surface of the support in the absence of the catalytic metal.

(3) Some important species or intermediates may not be detectable by transmission infrared, either due to their transient nature or to the location of the bands (e.g., masked by absorption of the support).

(4) Interpretation of the spectra may not be straightforward, especially if previously unidentified bands are produced.

The present work describes further infrared studies of supported ruthenium and iron catalysts under reaction conditions. The spectra presented will concentrate on bands observed in the hydrocarbon stretching region. Except for chemisorbed CO on ruthenium, which has been adequately described previously (*2, 3*), these are the only bands observed which can be attributed to surface species or "intermediates" attached directly to the metal site. By monitoring the surface at different reaction conditions (especially different temperatures), changes in the hydrocarbon bands are observed. This provides insight into important surface reactions and helps to resolve the previously observed differences between Fe and Ru catalysts.

EXPERIMENTAL DETAILS

Catalysts were prepared from $RuCl_3$ and $Fe(NO_3)_3$ hydrates dissolved in water at a concentration appropriate to yield the proper metal loading when impregnating with 1 ml solution per gram of support. The supports, silica (Davision 59) and alumina (CRE-1), were 20–60 mesh. The final catalysts were 1% Ru/Al_2O_3, 1.5% Ru/SiO_2, and 5% Fe/SiO_2 by weight. The freshly impregnated catalysts were dried under vacuum at 483 K for several hours. The catalysts were then ground to a fine powder, and 200 mg was pressed into a 1-in. self-supporting disk, which was subsequently trimmed to fit the catalyst holder (approx. dimensions 10 × 25 mm). Catalyst pretreatment was done *in situ*. This consisted of reduction in flowing H_2 at 373, 573, and 723 K for a period of 1 hr at each temperature. From previous studies (*4*), dispersions are estimated at 50% for Ru/Al_2O_3 and 15% for Ru/SiO_2. For the fresh Fe/SiO_2 catalyst, based on Vannice's work (*5*), dispersion is likely near 1%.

The infrared high pressure cell (*6*) comprised two main sections. The sample holder was attached to a transfer rod, and movement between the sections was accomplished hydraulically. The upper section consisted of a heater used mainly in catalyst pretreatment and was capable of temperatures exceeding 773 K. The lower section, as shown in Fig. 1, was made of a heavy-walled stainless-steel cylinder, 4 in. long, 1-$\frac{3}{8}$ in. i.d. Polycrystalline CaF_2 windows, 1-$\frac{5}{8}$ in. diameter and $\frac{1}{4}$ in. thick, were

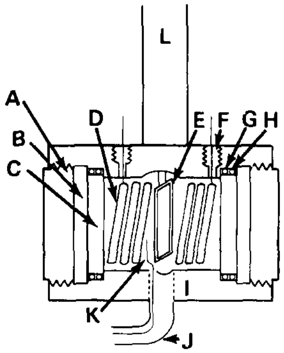


FIG. 1. Schematic of high-pressure cell: (a) threaded retaining ring; (b) blank with cutout; (c) CaF_2 polycrystalline window; (d) platinum-in-quartz coil heater; (e) sample and holder; (f) heater feedthrough; (g) viton O-ring; (h) Teflon ring; (i) cell body; (j) gas inlet tube; (k) thermocouple; (l) gas exit (to upper oven).

sealed by viton O-rings backed up by flat Teflon rings. Under pressure, the window plus ring arrangement pressed against stainless-steel blanks having cutouts for the light beam and in turn held by threaded rings. The actual gas path length within the cell was $1\text{-}\frac{3}{4}$ in.

Hydrogen and nitrogen gases were purified first by removal of oxygen (oxy trap) followed by passage over dry alumina. Hydrogen/carbon monoxide mixtures of 1/1 stoichiometry were purified by passage over 4A sieves, activated charcoal, and dry alumina. Due to the two section arrangement of the cell, a very small gas leak arose through the packing material surrounding the transfer rod. This leak was downstream of the reaction chamber and, since gases in the cell were flowing under pressure, this did not affect the infrared measurements. However, because of this arrangement, good vacuum within the cell could not be achieved. To remove or replace gases within the cell, a purging procedure was employed, consisting of successive pressurizing/depressurizing steps with the replacement gas.

The heating of gases within the lower cell was provided by a coiled platinum wire, enclosed except at the ends by sealed quartz tubing so that the hot portion of the wire was not exposed to reactant gases. Copper feed throughs were attached to the platinum and externally to a variac. The heater was capable of temperatures up to 573 K with atmospheric pressure H_2 or N_2, and somewhat lower temperatures at higher pressures due to convective heat loss to the walls of the cell. Cell wall temperature reached 353 K during some runs. A thermocouple fed through the bottom of the cell was located adjacent to the sample holder and monitored the catalyst temperature.

Spectra were recorded using a Beckman 4260 spectrometer interfaced to a small computer (Wang, Model 2200). This allowed accumulation and averaging of scans (to increase signal-to-noise ratio), subtraction of background spectra, and expansion of selected portions of the spectra. The infrared beam was chopped prior to the sample, in order to avoid complications from infrared emission from the hot samples. The spectrometer operated with a fixed slitwidth, with resolution approximately 15 cm^{-1} at 3000 cm^{-1}.

In order to eliminate contributions to the spectra from the support, blank runs were made. With Ru/SiO_2 and Fe/SiO_2, this blank consisted of replacing the H_2/CO feed with H_2 and rerunning the spectrum at comparable temperatures and pressures. This was made possible because no bands were observed from interaction of $CO + H_2$ with pure SiO_2 under reaction conditions. Such was not the case with Ru/Al_2O_3. As will be described in the next section, the hydrocarbon C–H region exhibited bands arising from $CO + H_2$ interaction with pure Al_2O_3 in the absence of ruthenium. In principle, a spectrum from pure Al_2O_3 could function as an appropriate blank; in practice, this was not satisfactory. In addition to problems arising from matching the blank with the sample (in order to make spectral subtraction meaningful), the bands on pure Al_2O_3 showed different intensities from Ru/Al_2O_3. For this reason, the majority of the data was obtained with the silica-supported catalysts.

INFRARED SPECTRA

Hydrocarbon C–H Stretch Region (3100–2700 cm^{-1})

The infrared cell was filled with H_2/CO at the desired pressure and a downstream valve was adjusted to allow gas flow at ~100 ml min^{-1} STP. The catalyst was then heated at a rate approximately 10–15°C min^{-1} until the desired temperature was reached. Following 5 min equilibration, infrared scans were then begun. Since multiple scans were made to improve signal-to-noise characteristics of the data, each spectrum was a composite of approximately 20–30 min of measurement at each temperature. No significant changes in intensity or shape of the bands were observed between the first and last scans at any temperature, implying nearly steady-state operation. The reaction temperature (or other conditions) was then changed and a new series of scans run. Additional experiments also showed that the spectrum observed at any temperature was independent of the previous temperature history, i.e., whether the given temperature was achieved by heating from a lower temperature or cooling from a higher one.

Ru/SiO₂. Figure 2 shows the spectra obtained in the 3100–2700 cm^{-1} (C–H) region with Ru/SiO_2 during H_2/CO reaction over a range of temperatures, following computer subtraction of the blank run. As a point of reference, the spectral features should be compared with product distributions from microreactor data (*4, 5*). At the lower temperatures, the prominent features are a pair of bands at 2930 and 2860 cm^{-1}. With increasing temperature, these bands become less prominent and seem to be replaced by a single broad band which peaks near 2935 cm^{-1}. The exact maximum of this band is poorly defined, but it shows some evidence of shifting to higher frequency with increasing temperature. In addition, a very prominent band appears at 3015 cm^{-1} at the higher temperatures, increasing with increasing temperature. Various experiments such as purging the cell or increasing the space velocity showed this band to be due to gas phase methane rather than a surface bound hydrocarbon. However, the remaining band near 2935 cm^{-1} showed little change under those conditions which produced a marked change in the methane band; it is attributable to surface bound species.

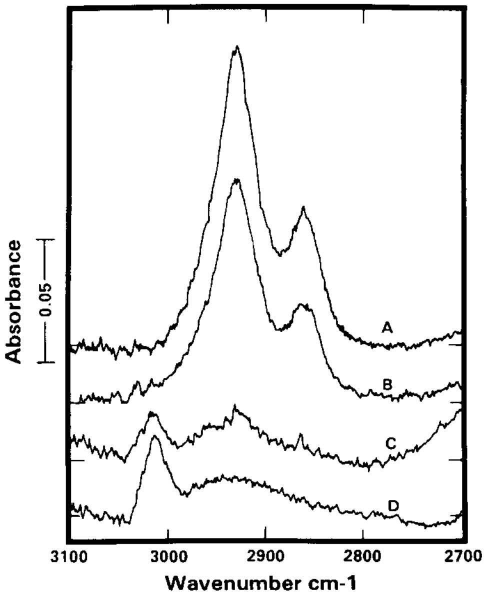


FIG. 2. Hydrocarbon formation during CO/H_2 reaction, Ru/SiO_2: (a) 428 K; (b) 463 K; (c) 503 K; (d) 528 K.

The bands observed at 2930 and 2860 cm^{-1} can be assigned to the asymmetric and symmetric stretches of saturated CH_2 groups (*7*). The relative strength of these bands compared to any underlying band at 2960 cm^{-1}, the expected position for CH_3 groups, suggests that the CH_2 species belong to relatively long hydrocarbon chains. The temperature dependence of these bands, i.e., their decrease with increasing temperature, parallels what is known about the temperature dependence of the chain length of Fischer–Tropsch hydrocarbon products with ruthenium (*4*).

The prominent CH_2 bands seen at the lower temperatures correspond to rather stable surface compounds rather than to transient species present only during reaction. This is demonstrated in Fig. 3. Ru/SiO_2 was reacted with H_2/CO at 498 K for 30 min in the pretreatment oven, followed by transfer to the spectrometer cell at ambient temperature while maintaining H_2/CO flow. The CH_2 bands in this case are narrower and more intense compared with the spectra obtained *in situ*. The latter effect is likely due to additional chain growth during radiative cooling of the catalyst, while the former probably reflects the effect of temperature on the broadness of the infrared bands. Since these bands are produced preferentially at temperatures lower than those normally employed for good H_2/CO conversion (*8*), they are not likely to be inter-

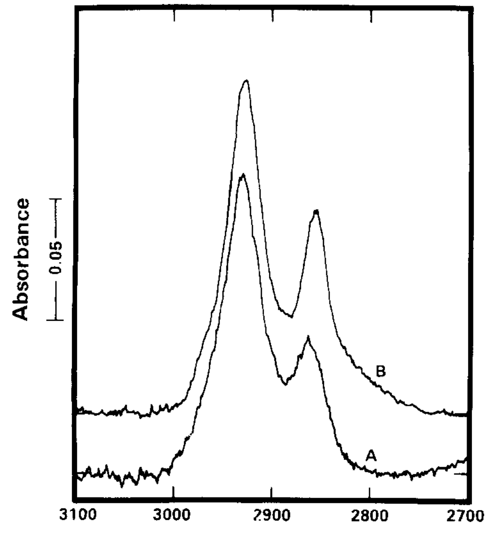


FIG. 3. Comparison of *in situ* with "quenched" spectra Ru/SiO_2: (a) *in situ* spectra from CO/H_2, 428 K; (b) CO/H_2 reaction at 498 K, followed by cooling to 300 K with flowing reactants.

mediates leading to gas phase products (i.e., C_1–C_4 hydrocarbons). The relation of these bands to the Fischer–Tropsch synthesis will be considered in the Discussion.

The broad band observed in this same region at higher temperatures is less easy to assign. It seems most likely, based on comparison with the lower temperature spectra, that this band arises from a mixture of CH_2 and CH_3 groups. The depleted band intensity at these higher temperatures reflects a marked decrease in hydrocarbon chain length. The broadness of the band and the shift to higher frequency could reflect an increased fraction of CH_3 groups, which terminate the hydrocarbon chain, or possibly even M–CH_3 species which could be hydrogenated directly to methane.

Ru/Al$_2$O$_3$. In contrast with Ru/SiO_2, hydrocarbon region spectra obtained with Ru/Al_2O_3 are more complicated. These are shown in Fig. 4. Similar to the lower temperature results from Ru/SiO_2, the main structure consists of a pair of bands at 2920 and 2850 cm^{-1} which can be ascribed to CH_2 species. In addition, there is a shoulder on the higher frequency band near 3000 cm^{-1}. With increasing temperature the 2850 cm^{-1} band disappears, while the 2920 cm^{-1} band decreases in intensity and shifts to lower wave numbers. The shoulder at 3000 cm^{-1} becomes more pronounced at the higher temperatures due to decrease of the 2920 cm^{-1} band, although it is not clear that the species absorbing at 3000 cm^{-1} has really increased in surface concentration. Various tests showed that these high-temperature bands correspond to surface bound species rather than gas phase products. Subsequently, a blank run with a pure Al_2O_3 support replacing Ru/Al_2O_3 was made. As shown in Fig. 4, bands near 3000 and 2900 cm^{-1} are produced on the Al_2O_3 blank. The strong high-temperature bands on Ru/Al_2O_3 are therefore not due to the presence of Ru, and thus are not related to hydrocarbon synthesis from CO and H_2. Also shown in Fig. 4 is the difference spectrum obtained by subtracting the high temperature (528 K) trace from the lower temperature one (443 K); this removes most of the contribution from reaction on the support, CO + H_2/Al_2O_3. The resultant looks similar to that obtained from Ru/SiO_2 at the comparable temperature.

Fe/SiO$_2$. The spectra obtained with the 5% Fe/SiO_2 catalyst at 150 psig H_2/CO be-

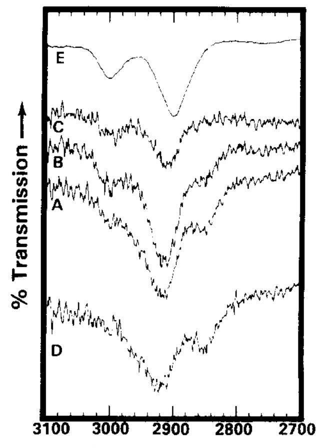


FIG. 4. Hydrocarbon formation during CO/H_2 reaction, Ru/Al_2O_3: (a) 443 K; (b) 503 K; (c) 528 K; (d) difference spectrum (a)–(c); (e) Al_2O_3 blank, 503 K.

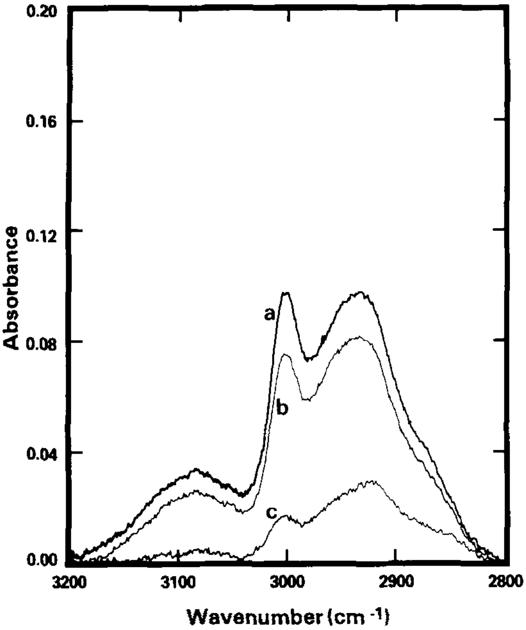


FIG. 5. Spectra obtained from 5% Fe/SiO_2 during reaction of H_2/CO = 1/1 at 150 psig, flowing: (a) 548 K; (b) 518 K; (c) 498 K.

tween 498 and 548 K are shown in Fig. 5. The spectra are very similar to those observed by Blyholder and Neff (*1*) (at a somewhat lower temperature). The spectra display the same general shape independent of temperature, although there is some variation in the relative intensity of the CH_4 band and the broader band near 2935 cm^{-1}. The relative intensity of the CH_4 peak increases with increasing temperature, as observed previously with Ru. The similarity between the Fe/SiO_2 spectra and the high temperature Ru/SiO_2 results (Fig. 2) is striking. However, the relative insensitivity of the 2935 cm^{-1} band shape to temperature with Fe/SiO_2 is significantly different from the Ru/SiO_2 catalyst described previously. While Ru/SiO_2 produces a strong pair of CH_2 bands at low reaction temperatures, no evidence was found for this with Fe/SiO_2. Rather, the single broad band remains throughout with Fe/SiO_2, but its overall intensity decreases markedly below 498 K. Only a very weak structure is seen below 2900 cm^{-1} with iron which could correlate with the 2860 cm^{-1} band on ruthenium. Clearly, long chain CH_2 structures are less prevalent on the iron surface.

The high quality of the Fe/SiO_2 spectra allowed additional information to be generated. By obtaining a spectrum of pure CH_4 at comparable resolution and ratioing its intensity to that observed during reaction, the contribution of the gaseous CH_4 band could be eliminated by computer subtraction. The resultant spectra are shown in Fig. 6, where they are compared with a spectrum obtained with Fe/SiO_2 under low pressure, fast flow reaction conditions. The former spectra show evidence of an additional band near 2995 cm^{-1}, arising from gas phase C_2^+ saturated hydrocarbons. These had been masked by the strong CH_4 band, but it is clear that C_2^+ hydrocarbon products are also produced under these synthesis conditions. By way of contrast, no evidence of

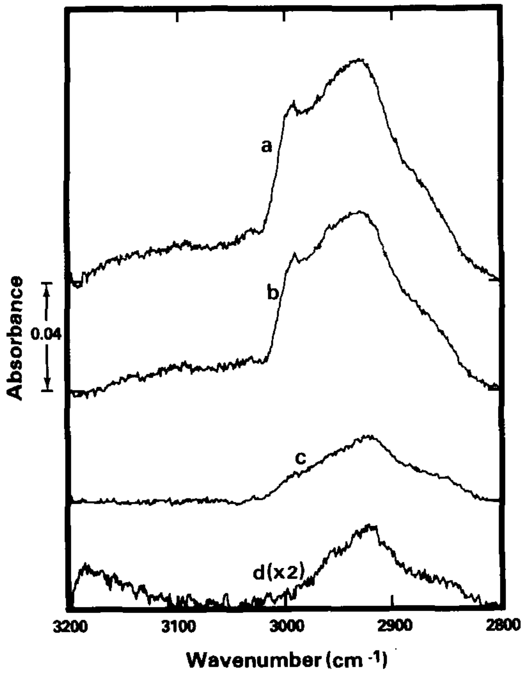
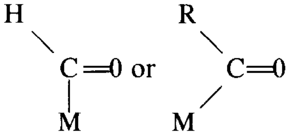


FIG. 6. Spectra 6(a), 6(b), and 6(c) are the same as 5(a), 5(b), and 5(c), respectively, except the spectral contribution from gas phase methane has been subtracted out by computer. Trace 6(d) is spectrum obtained from reaction at 578 K, 1 atm pressure, fast flow with Fe/SiO_2.

gaseous hydrocarbons is observed during the fast flow experiment (Fig. 6). This suggests that the broad 2930 cm^{-1} band observed in that case (as well as in the other spectra) corresponds to surface bound species.

Other Spectral Regions

In addition to the C–H stretch region, spectra were also obtained with the Ru/SiO_2 system in the range 2000–1300 cm^{-1} and 3900–3500 cm^{-1}. In the former region, spectra obtained during flow of H_2/CO over the catalyst showed no significant differences over a temperature range from 273 to 500 K other than a decrease in the tail of the CO band extending to 2000 cm^{-1}. Specifically, no band corresponding to a  $\mathrm{H{-}C({=}O){-}M}$ or $\mathrm{R{-}C({=}O){-}M}$ could be detected, even though under these conditions hydrocarbon bands of varying intensity could be seen quite readily. The 3900–3500 cm^{-1} (OH stretch) region contained a strong band corresponding to surface bound hydroxyl groups and chemisorbed water. Comparison of spectra obtained with H_2/CO and H_2 only on the Ru/SiO_2 catalyst at reaction temperatures showed that this band decreased with increasing temperature but was independent of whether H_2 or H_2/CO was present. Apparently, the rate of desorption of by-product H_2O under these conditions was fast relative to the rate of H_2O production from reaction. No other bands in this region were observed during reaction which could be attributed to OH bound to carbon containing intermediates. It is understood, of course, that such bands, if weak, could have been masked under the broad OH band from the silica surface.

The difference between the present results in the OH region and those of Blyholder (*1*) and Dalla Betta (*2*) deserve mention. Blyholder operated at a lower temperature in a closed nonflowing system where by-product water could accumulate on the surface. This is different from the present work in which accumulation of by-product water was prevented by higher reaction temperatures and flowing gases. Dalla Betta also demonstrated enhancement of the OH band during reaction over Ru/Al_2O_3 in a flowing system. Experiments in this laboratory confirmed this, suggesting stronger adsorption of by-product water on the Al_2O_3 surface compared to the SiO_2 surface.

DISCUSSION

Relation of Bands to CO Catalysis

Dalla Betta and Shelef (*2*) previously reported *in situ* spectra obtained from Ru/Al_2O_3. They observed hydrocarbon CH_2 bands similar to those reported here at the lower temperatures with ruthenium; these were ascribed to reaction products or by-products adsorbed on the alumina. There is no question that the high-temperature bands observed with Ru/Al_2O_3 are due to species adsorbed on Al_2O_3, since they are produced in the absence of Ru. However, it is not clear whether the CH_2 hydrocarbon bands observed with Ru/Al_2O_3 and also Ru/SiO_2 represent species attached to the support or to the metal. Dalla Betta and Shelef found that the CH_2 bands continued to grow even after the catalyst had reached steady state, implying that they were not active surface intermediates for the measurable gas phase products. However, this does not prove that these species are not attached to Ru or at least associated with reactions on Ru. Ruthenium is known to produce long chain hydrocarbons under certain conditions of temperature and pressure, with the distribution of products reflecting the competition between chain growth and chain termination. Once a hydrocarbon chain has achieved a certain critical length, it may become more difficult for it to desorb from the surface, even if termination occurs. It will, as a result, have an increased residence time in the catalyst bed, and may therefore be more likely to reattach at some point and undergo further chain growth, or polymerization (*9*). If the hydrocarbon chains become quite long, only a few such chains might be needed to account for the intense CH_2 bands observed.

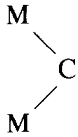
Some recent experiments by Caesar *et al.* (*10*) reinforce this argument, and suggest that the traditional concept of chain growth by Fischer–Tropsch catalysts needs to be modified. In those experiments, synthesis gas contacted an iron catalyst both with and without the admixture of a second zeolite component. In the absence of the zeolite, plugging of the catalyst bed by wax formation occurred. In the presence of the zeolite, no wax formation was observed. To explain this result, one must invoke a mechanism in which precursors to wax molecules, i.e., shorter chain hydrocarbons, are intercepted by the zeolite and undergo subsequent reactions which do not contribute to chain growth. Thus, the view that a final hydrocarbon product is formed on a single catalytic metal site may be incorrect. Rather, substantial migration and readsorption on subsequent sites may occur during the growth of a hydrocarbon molecule. Thus, to describe a species as either being bound to a metal site or to the support may not be possible, as it may tend to oversimplify a dynamic situation. Indeed, a relatively short chain product hydrocarbon may in a general sense be considered an "intermediate" to longer chain hydrocarbons, and thus to distinguish between adsorbed products and intermediates may be somewhat arbitrary.

Since the CH_2 bands observed at the lower temperatures are clearly not the intermediates for the primary gas phase products, the exact point of attachment may be unimportant; the intensity of the CH_2 bands is consistent with the tendency of Ru to form heavier hydrocarbons with decreasing temperature. As opposed to the lower temperature CH_2 bands, however, the single band near 2935 cm^{-1} at higher temperatures with Ru/SiO_2 and Fe/SiO_2 corresponds to species almost assuredly bound to the metal. The relative intensity of the CH_3 and CH_2 groups suggests short chain carbon–hydrogen species, which are not likely to be physisorbed on silica at such high temperatures. In addition, no evidence was seen in the present work for any increase in intensity of this band with time. This band is more likely to represent "intermediates" in the synthesis of short chain gas phase hydrocarbons, which are common to both Ru and Fe.

Temperature Dependence of the Hydrocarbon Bands

The spectra obtained with both the Ru and Fe catalysts during reaction suggest the presence of surface species containing only carbon and hydrogen. At temperatures above 500 K, the Ru and Fe traces look very similar, suggesting common surface species or intermediates. At temperatures below 500 K, ruthenium begins to produce long hydrocarbon chains, whereas iron does not. It is likely that this is related to the unique ability of ruthenium to produce paraffinic waxes at high pressures with H_2 and CO. The spectra thus suggest a stronger temperature dependence in the product distribution of Ru compared with Fe. This is borne out by the results of Vannice (*5*), who obtained activation energies for CH_4 production and total CO consumption with 1% Ru/SiO_2 and 5% Fe/SiO_2 catalysts. The difference in activation energies between methanation and total CO consumption is greater by a factor of two and one-half for ruthenium compared with iron. In addition, the absolute magnitude of these energies is greater by approximately a factor of three with ruthenium. This suggests a significant difference in the temperature dependence of the methane long chain hydrocarbon ratio for the two catalysts, with Ru being more temperature sensitive. This is in agreement with the spectral results presented here.

Mechanistic Considerations

Various mechanisms for CO hydrogenation over Group VIII metals have been reported in the literature (*9,11–14*). However, the evidence is becoming fairly strong that the initial step toward either methane or higher hydrocarbon synthesis on Ru, Fe, and Ni results from dissociation of CO to yield a surface carbide and oxide (*15–18*). The oxide is removed by reaction with H_2 or CO. Total hydrogenation of the surface carbon produces methane, but partial hydrogenation to species such as $M{=}CH_2$,  $\begin{matrix} M & \\ & \diagdown \\ & & CH_2 \\ & \diagup \\ M & \end{matrix}$, or $M{-}CH_3$ may also occur. These carbon–hydrogen species may then participate in chain growth by a mechanism that is not fully established. Ekerdt and Bell (*3*) have suggested that the surface of ruthenium becomes covered with carbon, and that in the absence of CO the surface can be reacted with gas phase hydrogen to produce small amounts of C_2^+ hydrocarbons as well as methane by polymerization of surface "carbenes." The role of CO is seen as a source of surface carbon and a "poison" toward hydrogen chemisorption which prevents the production of excessive methane. Recent experiments by Ekerdt and Bell (*19*), in which the active ruthenium surface is exposed to carbene or alkyl scavengers, has lent credence to the existence of partially hydrogenated carbon fragments on the surface during reaction, and the absence of CO insertion in the chain-growth step.

Recent work of Ponec (*20*) has also added credibility to the growth of hydrocarbons by carbene-type polymerization. A ruthenium catalyst exposed to ^{13}CO to produce a surface covered with ^{13}C was then reacted with $^{12}CO + H_2$, and the product was found to contain more than one ^{13}C in the product hydrocarbon chain. Evidence of chain growth by CO dissociation followed by a CH_x insertion step has also been provided in tracer studies by Biloen *et al.* (*21*). Thus, while chain growth by CO insertion cannot perhaps be excluded, evidence is strong that in many cases carbon–hydrogen surface species can undergo polymerization to higher hydrocarbons, and oxygen atoms need not be present in the surface complex.

The present infrared data are in substantial agreement with the above-mentioned results. The only infrared band other than CO observed at moderate reaction temperatures on the catalyst surface falls broadly over the CH stretch range, encompassing the region of both CH_2 and CH_3 species. It is most likely that both types of groups are present, and that the lack of structure reflects short chains, temperature broadening, and perhaps even mobility of these species on the surface. While the existence of surface acyl or enol species cannot be disproved (one can argue that these species are simply too transient to be observed), at least the existence of a surface carbide route seems to be well established. The alcoholic intermediate postulated by Blyholder and Neff can be explained better as a carbene plus surface H_2O. Thus, Fe and Ru behave similarly under hydrocarbon synthesis conditions. However, alcohols are known to be produced at higher pressures from iron catalysts but not from ruthenium (*22*). It is likely that, under those higher pressure conditions, oxygen-containing intermediates are on the iron surface. These may be observable with a sufficiently rugged infrared cell. The existence of such species deserves investigation.

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