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Characterization of a Fused Iron Catalyst for Fischer–Tropsch Synthesis by *in Situ* Laser Raman Spectroscopy

In situ laser Raman spectroscopy was used to characterize an alkali-promoted fused iron catalyst. Studies with adsorbed H_2 and CO revealed the presence of Fe—H and Fe—C bonds. Bands for adsorbed CO were also detected, indicating adsorption on Fe^0 and Fe^{n+} sites. Coexistence of Fe^0/Fe-carbide and Fe-oxide phases at the surface is proposed.

I. INTRODUCTION

The adsorption of CO/H_2 on various transition metals has been the subject of many previous studies, particularly in relation to Fischer–Tropsch synthesis (FTS). Among these transition metals, iron has attracted much interest because of its commercial use as a FTS catalyst.

It is well known that under steady-state FTS conditions, iron catalysts are converted to a mixture of bulk carbides and oxides. Only after this transformation occurs does the catalyst acquire the appropriate activity and selectivity (*1, 2*). This has led some workers to conclude that a carbide, rather than metallic Fe, is the actual catalyst for FTS (*3, 4*). An explanation for the transient behavior observed for iron catalysts during the period of carbide formation has been proposed (*5, 6*): when synthesis gas is admitted to a fresh catalyst, almost all of the CO quickly reacts to form iron carbide; only when the bulk of iron is more or less "saturated" with carbon is there some surface carbon available for FTS. These authors also report that precarbidation of iron catalysts with pure CO eliminates any induction period. It has also been possible to detect graphitic carbon on iron surfaces exposed to CO and H_2 using X-ray photoelectron spectroscopy (*7*), although this form of carbon may act as a poison (*8*). Evidence for the existence of oxidic phases has also been reported. Niemantsverdriet *et al.* (*9*) studied unsupported iron catalysts using Mössbauer spectroscopy. Iron oxide could be detected at low temperatures (4.2 K) after catalysts had been used for FTS. The iron oxide was believed to be present at the surface. Iron carbides could also be detected. Raymond *et al.* (*10, 11*) have reported recently that Fe_2O_3 prepared by the decomposition of iron nitrate is active for CO and H_2 (1 atm) conversion at 250°C even without any reduction pretreatment in H_2; Fe_3O_4 was proposed to be the catalytically active phase. However, some oxidation of these samples may have occurred prior to XPS measurements.

Despite the importance of iron as a FTS catalyst, a rather limited number of studies performed with modern spectroscopic methods has been reported. Investigations by Blyholder *et al.* (*12–15*) have involved CO adsorption and Fe/SiO_2 (infrared frequencies for adsorbed CO observed at 1925, 1980, and 2020 cm^{-1}) and on evaporated Fe films (infrared frequency for adsorbed CO observed at 1970 cm^{-1}). Dwyer and Somorjai (*16, 17*) have performed an AES study of iron catalysts following a prolonged period of FTS. Bonzel *et al.* (*18, 19*) used AES and XPS to study iron foils and iron (110) single crystals which had been exposed to CO/H_2 at elevated temperatures.

In order to gain further insight into the nature of FTS, more detailed information is needed about the composition of the active catalyst and about the adsorption and acti-

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vation of reactant molecules on the surface under actual reaction conditions. In this respect, *in situ* spectroscopic techniques possess a decided advantage in that they are applicable at the elevated temperatures and pressures used in FTS. Laser Raman spectroscopy is a promising alternative to infrared spectroscopy for studying samples with poor infrared transmittance—such as the iron catalysts used in FTS.

In the present research, *in situ* laser Raman spectroscopy has been applied to the investigation of CO/H_2 adsorption on an alkali-promoted fused iron catalyst. The Raman spectra, which were obtained under actual reaction conditions for FTS, provide new information about the nature of the active phase of the catalyst and about the reaction pathway for FTS.

II. EXPERIMENTAL PROCEDURE

The alkali-promoted fused iron catalysts used in this investigation were produced by heating a mixture of magnetite (Fe_3O_4), K_2O (1%), and Al_2O_3 (3%) in an electric arc furnace to 1500°C. The catalyst sample was ground to a fine powder and then was pressed into a pellet for Raman spectroscopic examination (weight of 0.8 to 1.0 g and diameter of $\frac{1}{2}$ in. compressed for 3 min under 12,000 lb pressure). Samples were mounted in a controlled-atmosphere quartz cell, which was designed similarly to those discussed by Schrader and Hill (*20*) and Cheng and Schrader (*21*). Prior to obtaining the Raman spectra, samples underwent a reduction pretreatment in the spectroscopic cells using a flow of purified H_2 under the following conditions: 120°C for 2 h, 250°C for 2 h, 350°C for 8 h, and finally 450°C for a minimum of 24 h, The surface area of the reduced catalyst was 15 m^2/g, as determined by BET methods (Micromeritics 2100E AccuSorb).

Gaseous H_2 (Matheson, UHP, 99.999%) and CO (Matheson, CP, 99.5%) were purified by passing through a Deoxo purifier and then through a 5-Å molecular sieve trap.

A Spex Industries 1403 Raman spectrometer was used in these studies. The 514.5-nm line from a Spectra Physics Model 164 argon ion laser was used for excitation, with an intensity of about 400 mW at the source. Slit width settings corresponded to a resolution of 4 cm^{-1}. The spectrometer was interfaced with a Nicolet 1180E data system. Spectral accumulation was necessary; up to 60 scans were accumulated in some cases to obtain an acceptable signal-to-noise ratio.

After the catalyst had been exposed to a flow of a $5H_2/1CO$ mixture, Raman spectra were taken *in situ* at 200°C or after cooling down to room temperature.

III. EXPERIMENTAL RESULTS

(A) *Raman Characterization of H_2 Adsorption*

Figure 1a is the Raman spectrum (region 1250–2150 cm^{-1}) of hydrogen species adsorbed on the prereduced iron catalyst after 48 hr of reduction by H_2 at 450°C, followed by cooling to 200°C in a flow of H_2 (flow rate of 3600 ml/h). Bands are present at 1625 (m), 1902 (m), and 1951 (s) cm^{-1}. The region at 1850–2150 cm^{-1} of this spectrum corresponds closely to our spectrum reported for hydrogen adsorption on the same catalyst at 400°C (*22*). It has been indicated that adsorption of H_2 on transition metals is dissociative, nonactivated, and mobile above about −100°C (*23–27*). For terminally bonded H in most transition metal molecular clusters, M—H stretching frequencies appear in the region 1850–2000 cm^{-1} (*28, 29*). However, for bridging H species, bands are observed at lower frequencies, and band intensities are altered significantly. Strong bands are generally observed for terminally bonded species while weak bands are apparent for multicentered bonding modes. For several cluster compounds, bridging H modes have bands in the region of 1245–1680 cm^{-1} (*26*); the intensities of these bands are very sensitive to temperature and greatly decrease with increasing

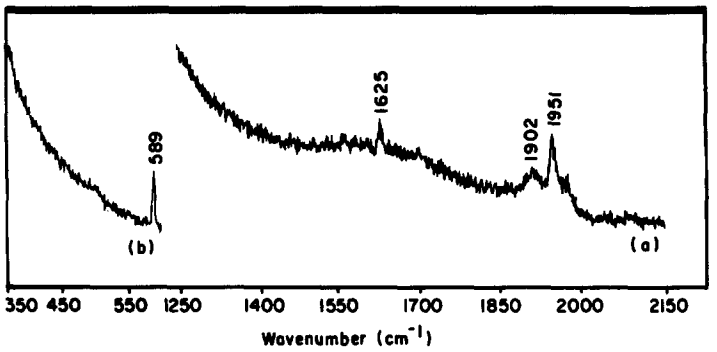

FIG. 1. (a) Raman spectrum (region 1250–2150 cm^{-1}) of the alkali-promoted, fused iron catalyst after 48 h of reduction by H_2 at 450°C and subsequent cooling to 200°C; the spectrum was taken *in situ* at 200°C in flowing H_2. (b) Raman spectrum (region 350–600 cm^{-1}) of the fused iron catalyst after 48 h of reduction by H_2 at 450°C and subsequently cooling to room temperature.

temperature. Thus, the Raman bands at 1902 and 1951 cm^{-1} shown in Fig. 1a may be assigned to Fe—H stretching vibrations due to terminally adsorbed H species, as we have discussed for a similar system (*22*). The band at 1625 cm^{-1} could be reasonably ascribed to a Fe—H stretching mode for bridging H species.

Figure 1b is the Raman spectrum of the same sample in the region 350–600 cm^{-1} at conditions under which detection of Raman bands is optimal (static gas atmosphere at room temperature). Except for a weak peak at 589 cm^{-1} (which has been identified to be due to the Si—H stretch for hydrogen atoms adsorbed on the quartz window of the sample cell (*30*)), there are no new significant Raman spectral features.

(*B*) *Raman Spectra of CO/H₂/Fe System*

To gain information about adsorbed species which might exist on the iron catalyst under reaction conditions associated with FTS, a sample of the prereduced (450°C for 60 h) iron catalyst was exposed at 200°C to a mixture of $5H_2/1CO$ at a flow rate of 7200 ml/hr for 60 min. The sample was then cooled to room temperature in the feed flow. In the region 1550–2350 cm^{-1} shown in Fig. 2a, bands appeared at 1556 (m), 1820 (w), 1902 (w), 1951 (s), 1975 (m), 2080 (m), 2160 (m), 2175 (m), and 2331 (m) cm^{-1}. As has been previously indicated (*22*), the 2331-cm^{-1} band can be ascribed to the stretching vibration of gaseous N_2 in the external sample compartment area of the Raman spectrometer. The existence of a considerable amount of dissociatively adsorbed hydrogen on the surface of the catalysts has been identified by several investigators (*28–30*). Raman bands at 1951 and 1902 cm^{-1} were apparent for H_2/Fe systems at the same temperature (Fig. 1a); the bands in Fig. 2a corresponding to the same frequencies are attributed therefore to Fe—H stretching modes for adsorbed hydrogen.

Except for the Fe—H bands, the Raman spectrum is somewhat similar to the corresponding infrared spectrum of CO/H_2 adsorbed on SiO_2-supported iron as reported by Blyholder and Neff (*13*). Bands at 1975, 2080, 2160, and 2175 cm^{-1} are probably due to C≡O stretching vibrations corresponding to several terminally adsorbed CO species, which exist perhaps on different adsorption sites. The large shift from 2143 cm^{-1} for the gaseous CO molecule to 1820 cm^{-1} for chemisorbed CO implies multinuclear coordinated activation of the carbon–oxygen triple bond. In this configuration strong electron back-donation from the transition metal active site to the adsorbed CO molecule would result in significant weakening of the triple bond. This form of

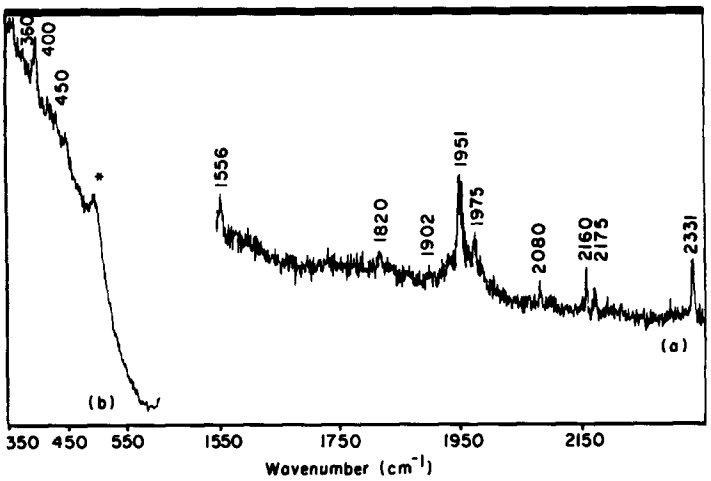

FIG. 2. (a) Raman spectrum (region 1550–2350 cm^{-1}) of species adsorbed on the fused iron catalyst after 60 min of exposure at 200°C to a flow of $5H_2/1CO$ mixture at a flow rate of 7200 ml/cm^3 catalyst · h (STP) and then cooling to room temperature. (b) Raman spectrum (region 350–600 cm^{-1}) of species adsorbed on the fused iron catalyst after 60 min of exposure at 200°C to a flow of $5H_2/1CO$ mixture at a flow rate of 7200 ml/cm^3 catalyst · h (STP) and then cooling to room temperature (* peak due to quartz window).

chemisorbed CO might be a precursor of dissociated CO. The 1556-cm^{-1} band is likely due to an oxygenated intermediate, probably a formate-like species, as has been discussed by several workers (*13, 34–38*). Blyholder and Neff (*13*), however, attributed this band to a metal–oxide catalyst structure.

The Raman spectrum for the region 350–600 cm^{-1} is shown in Fig. 2b, in which Raman bands are present at 360, 400, and 450 cm^{-1}. These bands may be reasonably attributed to vibrations concerned with Fe—C bonds corresponding to adsorbed CO species (*11, 14, 16*).

The previous data involved cooling the sample to room temperature so that reaction conditions may have been perturbed. However, an *in situ* study at actual reaction conditions for FTS provides direct information concerning the existence of these species on the surface of the functioning catalyst.

Following H_2 prereduction at 450°C for 48 h, a fused iron catalyst sample was cooled to 200°C in flowing H_2; at this temperature, a feed of $5H_2/1CO$ was introduced at a flow rate of 9000 ml/h. After 3 h of exposure, the Raman spectrum of the functioning catalyst was recorded *in situ*. Figure 3 shows an accumulation of 40 scans in a duration of 250 min. Bands are present at 1556 (m), 1820 (w), 1850 (w), 1890 (m), 1902 (w), 1948 (s), 1970 (w), 2070 (m), 2130 (m), 2143 (w), 2160 (m), and 2175 (w) cm^{-1}. In comparing this spectrum with the spectrum obtained at room temperature, it is apparent that the major spectral features are similar, although some variation in the positions and intensities of the bands is observed. In addition, an unusually broad band appeared in region 1586–1660 cm^{-1} for the elevated temperature spectrum. The 1948- and 1902-cm^{-1} bands are assignable to Fe—H species. Bands at 1970, 2070, 2130, 2160, and 2175 cm^{-1} are ascribed to several terminally adsorbed CO species; the 1820-, 1850-, and 1890-cm^{-1} bands are due to multinuclear-coordinated CO species. The 2143-cm^{-1} band is attributed to gaseous CO. The 1556-cm^{-1} band and region 1586–1600 cm^{-1} are probably indicative of oxygenated intermediates.

All Raman bands observed for these

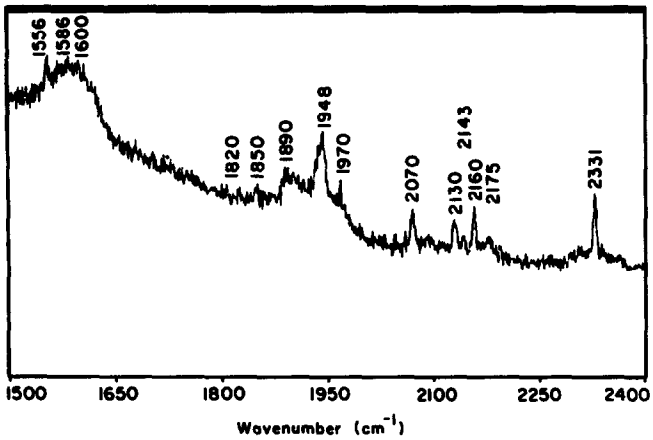

FIG. 3. *In situ* Raman spectrum (region 1500–2400 cm^{-1}) of adsorbed species on the functioning fused iron catalyst at 200°C in a flow of $5H_2/1CO$ feed gaseous mixture at a flow rate of 9000 ml/cm^3 catalyst · h (STP).

studies and the proposed assignments are summarized in Table 1. The valence of Fe associated with the adsorption sites listed in Table 1 are discussed in the following section in connection with the nature of the catalytically active phase. The results of this Raman spectroscopic investigation have useful implications concerning the nature of the active phase of the catalyst and the general understanding of the reaction mechanism.

IV. DISCUSSION OF RESULTS

Previous studies of Fe-based catalysts for FTS have shown that the chemical composition of the catalysts changes noticeably during use and that the surface layers and the bulk of the catalysts may exist as different phases (*2, 4, 16, 19, 38*). The investigations conducted by Loktev *et al.* (*39, 40*) have shown that the activity and selectivity of a fused iron catalyst are unchanged over hundreds of hours despite marked changes in the composition of the bulk phase (initially consisting of 85% α-Fe, but finally comprised of 65% Fe_3O_4, 25% iron carbides, and 8% α-Fe). These authors concluded that the activity of the catalyst is not related to the presence of bulk iron oxides and carbides; rather, a nonoxidized surface layer with a defect iron carbide structure is responsible for the catalysis. Iron oxides and carbides existing in the bulk phase serve only as carriers, and a broad variation of their concentration in the catalyst does not dramatically affect catalytic activity.

TABLE 1

Assignment of Raman Bands for Adsorbed Species Associated with Fischer–Tropsch Synthesis on an Alkali-Promoted, Fused Iron Catalyst

Band position (cm^{-1})	Assignment
1951 (1948), 1902	Fe—H stretch of terminal H species
1625	Fe—H stretch of bridging H species
1970	C—O stretching of CO adsorbed on Fe^0 sites
2070	C—O stretching of CO adsorbed on Fe^{2+} sites
2130, 2160, 2175	C—O stretching of CO adsorbed on Fe^{3+} sites
1820, 1850, 1890	C—O stretching of CO adsorbed to form multinuclear Fe^0 clusters
1556, 1586–1600 region	Vibrations due to formatelike species
360, 400, 450	Fe—C stretch of adsorbed CO species

The formation of iron oxide phases during FTS can be confirmed by the results of our Raman spectroscopic investigation. The stretching frequencies of adsorbed CO serve as a sensitive probe of the surface of the catalyst. Changes in the binding of CO to the surface metal atoms as a function of the surface structure and composition can be examined.

Using an industrial iron–chromium con-

version catalyst (Fe/Cr = 91/9) which had been oxidized, Rubene *et al.* (*34*) observed IR bands at 2120, 2140, and 2175 cm^{-1}; weak maxima were also observed at 1920, 2045, and 2095 cm^{-1}. After the sample was heated for 2 h in CO at 250°C, a decrease in band intensities at 2120, 2140, and 2175 cm^{-1} occurred, while an increase in band intensities at 1920, 2045, and 2095 cm^{-1} was detected. This result indicated that the former three bands may be related to CO adsorption on oxidized surface sites, probably Fe^{3+} sites. The latter three bands may be due to CO adsorption on deeply reduced and/or partially reduced surface sites, perhaps Fe^0 or Fe^{2+} sites. More recently, analogous behavior has been detected by King and Peri (*41*) in their IR studies characterizing unpromoted and potassium-promoted Fe/Al_2O_3 catalysts using NO as a probe molecule. Coexistence of Fe^{3+} and Fe^0 has also been demonstrated in an ESCA investigation by Raymond *et al.* (*42*) using an alkali-promoted, fused iron catalyst which had been exposed 1 h to $9H_2/1CO$ at 250°C. Benziger and Larson (*43*) used infrared spectroscopy to study the adsorption of CO on a Fe/MgO catalyst and on a metallic Fe, FeO, and Fe_2O_3. Assignments of the observed IR bands were as follows: the 2175-cm^{-1} band for Fe_2O_3 powder and the 2150-cm^{-1} band for unreduced Fe/MgO are due to Fe^{3+}-CO; the 2100-cm^{-1} band on FeO powder and the 2070-cm^{-1} band on partially reduced Fe/MgO are assigned to Fe^{2+}-CO; the 1960-cm^{-1} band on metallic Fe powder and the 1965-cm^{-1} band on deeply reduced Fe/MgO are ascribed to Fe^0-CO; the 2020-cm^{-1} band on deeply reduced Fe/MgO is due to CO adsorbed on very small clusters of iron, producing an adsorption state resembling iron carbonyls. The IR bands observed by Benziger and Larson are in good agreement with the Raman bands which we have observed and therefore are assigned to terminally adsorbed CO species.

According to the work of the groups mentioned above, the observed five Raman bands for adsorbed CO may be assigned in detail as follows: the 2130-, 2150-, and 2175-cm^{-1} bands are assigned to CO adsorbed on Fe^{3+} sites with different local environments; the 2070-cm^{-1} band is associated with Fe^{2+}-CO; and the 1970-cm^{-1} band is due to Fe^0-CO.

The Raman spectra obtained in this work can be interpreted as giving evidence for the existence of the iron oxide phase on the surface of the functioning fused iron catalyst. Moreover, it was observed that after several hours of FTS conditions, an increase in the intensities of the bands at 2070, 2130, 2160, and 2175 cm^{-1} and a decrease in the intensity of the band at 1970 cm^{-1} occur simultaneously (comparing Fig. 3 with Fig. 2a). This also indicates that the iron oxide surface phase develops during the "break-in" of the prereduced catalyst. Therefore, our results indicate that the oxide phase exists on the surface and not only in the bulk, as was shown by Loktev *et al.* (*39, 40*). Coexistence of this phase with α-Fe and iron carbide phases is likely.

These results indicate that chemisorption and activation of CO takes place not only on Fe^0 sites but also on Fe^{n+} sites. On the Fe^0 sites, adsorbed CO may undergo a transformation from a "perpendicular" terminal coordination (Raman band observed at 1970 cm^{-1}) to an "inclined" bonding mode involving multinuclear coordination (Raman bands observed at 1820, 1850, and 1890 cm^{-1}). Subsequently, the adsorbed CO can be dissociated into atomically adsorbed species, C(a) and O(a). On the Fe^{n+} sites, adsorption of CO is probably nondissociative and terminal (Raman bands observed at 2070, 2130, 2160, and 2175 cm^{-1}). Activation of the carbon–oxygen triple bond—which is not sufficient to lead to bond breaking—can lead to the hydrogenation of CO to oxygenated products.

The formation of oxygenated hydrocarbons on transition metal catalysts has been studied by other researchers. Somorjai *et al.* (*44, 45*) examined well-defined Rh surfaces under CO/H_2 conversion conditions

and made several important observations: pure, carefully reduced, and unsupported Rh was active only for the formation of hydrocarbons; oxygenated products appeared when Rh was preoxidized. These authors believed that the promotional effect is due to oxygen present in the Rh^0 metal and that the modified metal is the active center for the hydrogenation of CO to oxygenates. However, according to the work by Iwasawa *et al.* (*46*), it has been suggested that Rh^{n+} sites actually are more likely to be the active sites for oxygenate formation. Analogous behavior seems to also occur on iron catalysts used in this study. Since iron oxide is active for the reaction of CO and H_2 (at 250°C, 1 atm) even without any prereduction in H_2 (*10, 11*), the presence of a reduced metal (Fe^0) is probably not a necessary condition for the formation of alcohols. Therefore, it seems to be more likely that two types of active phase coexist on the surface of the iron catalyst for FTS: a Fe^0/Fe-carbide phase and an Fe-oxide (probably Fe_3O_4) phase. Under steady reaction conditions, these two active phases are in equilibrium with gaseous CO, H_2, CO_2, and H_2O. The relative concentrations clearly depend on the specific reaction conditions. A high reaction temperature and a high ratio of H_2/CO in the feed gaseous mixture may be expected to inhibit the formation of the Fe-oxide phase on the surface of the catalyst. The carbide phase may be responsible for adsorption, activation, and dissociation of CO; methane and higher hydrocarbons are probably the dominant products. For the oxide phase, the active center may be a relatively low-valent metal ion, such as Fe^{2+}, on which adsorbed CO is activated and further hydrogenated via an intermediate [$C_1H_xO_y$(a)] to methanol; alkyl groups from nearby Fe^0/Fe-carbide active sites may be converted into oxygenated products by insertion of the $C_1H_xO_y$(a) species. The observed Raman bands in the region 1560 to 1600 cm^{-1} (Fig. 3) may be interpreted as providing evidence for such a $C_1H_xO_y$ intermediate.

V. CONCLUSIONS

The Raman spectroscopic studies on an alkali-promoted, fused iron catalysts indicate that, under actual reaction conditions for FTS ($5H_2$/1CO, 1 atm, 200°C), chemisorption and activation of CO take place not only on Fe^0 sites but also on Fe^{n+} sites. There may exist two active phases operating simultaneously on the surface of the iron catalyst: Fe^0/Fe-carbides and an Fe-oxide.

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