JOURNAL OF CATALYSIS **79**, 164–175 (1983)

An Infrared Study of Nitric Oxide Chemisorption on Alumina-Supported Iron and Alkalized Iron Fischer–Tropsch Catalysts

D. L. KING[1] AND J. B. PERI

Amoco Oil Company, Research and Development Department, P.O. Box 400, Naperville, Illinois 60566

Received July 8, 1982; revised October 1, 1982

The chemisorption properties of unpromoted and potassium-promoted iron catalysts were studied by infrared spectroscopy using nitric oxide as a probe molecule. The catalysts, supported on alumina, are active in the Fischer–Tropsch synthesis, producing increasing fractions of long-chain hydrocarbons and olefins with increasing alkali content. The NO chemisorption spectra on the reduced catalysts are complex, but major features include bands indicative of Fe^{2+} and Fe^0 sites. On oxidized catalysts, the band ascribed to Fe^0 disappears, while bands corresponding to more oxidized species such as nitrates or nitrites are evident. With increasing alkali loading, the major NO bands exhibit a shift to lower frequencies. With the reduced catalysts, increasing the potassium loading results in a decrease in the Fe^0 band and an increase in the more oxidized NO species. In the presence of gas-phase H_2, the NO band corresponding to Fe^0 is substantially greater with these same catalysts. The results are interpreted in terms of the electron donor properties of potassium on the iron catalyst surface. It is suggested that a delicate balance exists between associative and dissociative chemisorption of NO with these catalysts.

INTRODUCTION

Iron-based catalysts have, for many years, occupied a dominant position in the synthesis of hydrocarbons and oxygenates from CO and H_2. The attractiveness of iron as a Fischer–Tropsch catalyst arises both from its low cost and from the wide range of products which can be synthesized. Despite the years of research, the nature and function of the various phases on the catalyst surface, for example, carbides, oxides, and reduced iron, are still not defined although progress has been made (*1*, *2*). As a further complication, pure iron is not a good CO hydrogenation catalyst, and a variety of promoters must be mixed with the iron to enhance such properties as catalyst surface area, temperature stability, and product selectivity (*3*).

The number of promoters used with a typical iron Fischer–Tropsch catalyst are so numerous that fundamental research aimed at detailed understanding of the catalyst surface appears to be unrealistic. As a simplifying assumption, promoters have been considered to function in one of three ways: to enhance structural integrity (Al_2O_3, SiO_2, ThO_2, other difficult-to-reduce oxides); to promote low-temperature reduction (Cu); and to increase activity and alter selectivity (K_2O) (*3*, *4*).

Alkali appears to be the only promoter to markedly alter the product distribution. Addition of potassium oxide increases the average hydrocarbon chain length and olefin yield while decreasing the selectivity to methane. Alkali is thought to alter the iron surface by increasing the strength of chemisorption of CO while decreasing the ability of the surface to dissociatively chemisorb H_2 (*5*). The net result is the enhancement of products of lower H/C ratio.

Infrared spectroscopy provides a potential tool to monitor the interaction of the promoted iron catalyst surface with various absorbates. Probe molecules such as CO or

---

[1] Present address: Catalytica Associates, Inc., 3255 Scott Boulevard, Bldg. 7-E, Santa Clara, California 95051.

0021-9517/83/010164-12$03.00/0

NO are sensitive indicators of the nature of the adsorption site. Shifts in the stretching frequencies of these molecules with a series of related catalysts can provide information on the variation in charge density of the site and, indirectly, on their binding strength with the surface (*6*). By observing changes in adsorption properties of CO or NO following addition of varying amounts of potassium oxide to the iron catalyst surface, it may be possible to gain insight into the nature of the promotional effect. Of necessity, these iron catalysts must be supported, due to the inability of a bulk iron catalyst to transmit infrared radiation.

Despite the obvious appropriateness of CO as a probe of the iron catalyst surface (since it is a Fischer–Tropsch reactant), it is not a useful adsorbate with iron. With the exception of infrared studies of Blyholder and Neff using iron catalysts immersed in oil (*7*), attempts to observe CO chemisorbed on supported iron catalysts have been largely unsuccessful, although some bands may be produced at high CO pressures (*8*). This may be related to problems in obtaining clean, reduced surfaces (*9*). To overcome the difficulty encountered in observing CO bands on supported iron catalysts, NO was selected for this study as an alternate probe molecule. Unlike CO, NO was found to readily chemisorb nondissociatively on supported iron, producing a variety of intense bands.

This study consists of two parts. In the first part, alumina-supported iron catalysts having different K_2O contents are compared for the CO–H_2 reaction using a fixed-bed microreactor. This is to demonstrate qualitatively that the alkali treatments do indeed alter the selectivity of the supported iron catalysts toward the Fischer–Tropsch synthesis in a manner similar to that observed with unsupported iron. In the second part, these same catalysts will be characterized by NO chemisorption using infrared spectroscopy, following a variety of pretreatments. The spectroscopic results, which provide information on catalyst surface properties, will be compared with actual catalyst performance.

METHODS

Catalysts were prepared by impregnation of 20- to 40-mesh γ-alumina (PHF) with a solution of ferric nitrate. The solution was at a concentration such that 1 ml of solution was used per gram of support to produce a 10% Fe (by weight) catalyst. Following vacuum drying at 383K for 2–4 h, portions of the iron catalyst batch were reimpregnated with an aqueous solution of potassium carbonate at one of three different concentrations. The resulting catalysts contained, in addition to iron, 1.0, 1.5, and 2.0% by weight potassium. This catalyst was again vacuum dried at 383K for 2–4 h and calcined overnight at 773K. This sequential impregnation resulted in a more active catalyst than when iron and potassium were co-impregnated on the alumina. Initial impregnation with potassium salt solution followed by impregnation with iron solution produced catalysts having poor activity.

For the microreactor studies, the dried catalysts were tested in a fixed-bed, downflowing stainless-steel reactor. Details of the reactor have been presented previously (*10*). The catalyst charge of 1.2 g was pretreated with flowing He for 1 h at 573K, followed by flowing H_2 for 1 h each at 573 and 773K. Following pretreatment, synthesis gas, first purified by passage through molecular sieve traps, was fed over the catalyst. Gas chromatographic measurements were made 20–30 min subsequent to the initiation of synthesis gas flow. At that time, an approximate steady state was obtained with minimal catalyst deactivation. Before changing reaction temperature, the catalyst was re-reduced in flowing H_2 at 773K for 1 h. Gaseous reaction products were measured (C_1–C_4 hydrocarbons, C_5 saturated hydrocarbons, CO_2) along with unconverted CO using a Carle Model 8500 Basic Gas Chromotograph, which was standardized with calibrated gas mixtures.

For the infrared studies, the same catalysts used in the reactor studies were ground to a fine powder, and 200 mg was pressed into a 1¼-in.-diameter wafer. This wafer was trimmed to fit a rectangular catalyst holder and placed in an evacuable quartz infrared cell equipped with calcium fluoride windows. Pretreatment of the catalyst consisted of heating for 1 h at 573K under vacuum, reduction for 1 h each at 573 and 773K in 10 Torr H_2, and evacuation at 773K. Any subsequent pretreatments are as described in the following section. Infrared spectra were obtained with a Beckman 4260 spectrometer, interfaced to a Wang Model 2200 computer. Good quality spectra were obtained by averaging multiple scans. Other operations, such as scale expansion or spectra subtraction, were also handled by the computer. All spectra were obtained in the double-beam mode, with a fixed slitwidth which was adjusted according to sample opacity. Typical resolution was 6 cm^{-1}.

Nitric oxide was obtained commercially and purified by several freeze–pump–thaw cycles. Hydrogen, used both for reduction and in co-absorption experiments, was purified by passage through palladium membrane. High-purity oxygen was used without further purification.

MICROREACTOR RESULTS

Four 10% Fe/Al_2O_3 catalysts, containing 0, 1.0, 1.5, and 2.0 wt% potassium as K_2O, were tested for hydrocarbon synthesis at 548 and 573K, at constant pressure (75 psig), H_2/CO ratio (*2*), and gas space velocity (900 h^{-1}). The H_2/CO conversions were not obtained in these experiments, since the microreactor was not equipped to measure liquid hydrocarbon products or gas contraction. However, conversions are roughly estimated at 5–10% at 548K, and 15–25% at 573K. Increasing the space velocity at the 573K reaction temperature showed little change in product distribution, suggesting minimal complications arising from heat or mass-transfer effects. Qualitatively, the 10% Fe/Al_2O_3 catalyst was the most active for hydrocarbon production at 548K; at 573K, the 10% Fe/1% K/Al_2O_3 catalyst had the highest activity.

The C_1–C_4 hydrocarbon product distributions which were obtained at 573K with the four catalysts are shown in Fig. 1. The ordinate scale in the figure, wt% product, is arbitrarily normalized to the total hydrocarbon product measured, which included the saturated C_5 hydrocarbons. Clearly, inclusion of the total hydrocarbons produced (C_5^+) but unmeasured would reduce the nu-

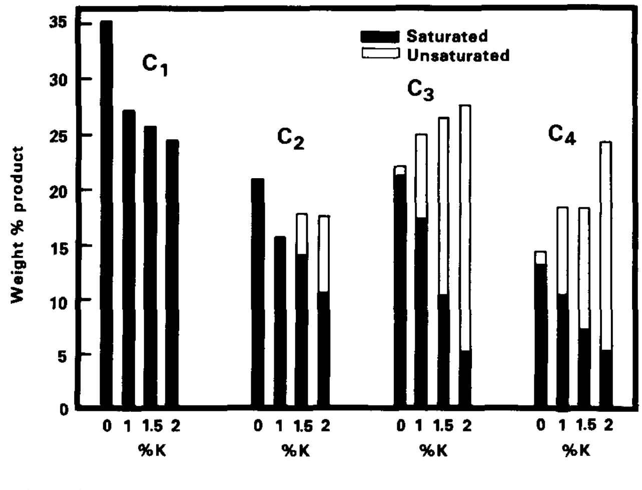

FIG. 1. Distribution of C_1–C_4 hydrocarbon products from 10% Fe/Al_2O_3 catalysts containing 0, 1, 1.5, and 2% potassium as K_2O at 573K.

merical value of the C_1–C_4 weight fraction in Fig. 1. However, the important qualitative conclusions which can be drawn remain: with increasing alkali loading the methane selectivity decreases, the C_3–C_4 selectivity increases, and the olefin content of the product increases. A similar trend was found at 548K. These results are in qualitative agreement with the selectivity patterns observed with unsupported iron catalysts as a function of alkali loading and temperature (*3*, *4*). This suggests that the promotional effect of alkali is similar in the two cases, and that supported alkalized iron catalysts can serve as satisfactory models for commercial unsupported iron Fischer–Tropsch catalysts.

It must be stressed that the comparison between unsupported and supported catalysts must remain qualitative, especially

TABLE 1

Summary of Infrared Results

Pretreatment	Catalyst	Major bands in cm^{-1} (assignment)	Comments
H_2, 773K; evacuation	10% Fe/Al_2O_3	1800, NO on Fe^{2+}; 1720, NO on Fe^0	1800-cm^{-1} band indicates strongly held NO.
	10 Fe/1% K/Al_2O_3	1780, NO on Fe^{2+}; 1710, NO on Fe^0	Similar to alkali-free catalyst, with small shift to lower frequencies and greater band intensity.
	10% Fe/1.5–2% K/Al_2O_3	1780–1770, NO on Fe^{2+}; 1700, NO on Fe^0; 1550–1450 nitrite complex; 1280–1200 nitrite ion	Bands indicating NO chemisorption are drastically reduced in intensity with some further shifting of bands to lower frequencies. Bands at lower frequencies indicate NO oxidation to nitrate or nitrite. Strongly held NO decreases with increasing K_2O content.
O_2, 773K; evacuation	10% Fe/Al_2O_3	1810, NO on Fe^{2+}	Lower-frequency weak bands indicate oxidized NO.
	10% Fe/1% K/Al_2O_3	1800, NO on Fe^{2+}	Similar to alkali-free case; small band shift to lower frequency.
	10% Fe/1.5–2% K/Al_2O_3	1790–1780, NO on Fe^{2+}	Drastic decrease in intensity of NO bands; oxidized NO species below 1600 cm^{-1} lower in intensity than with alkali-free catalyst.

TABLE 1—*Continued*

Pretreatment	Catalyst	Major bands in cm^{-1} (assignment)	Comments
H_2, 773K; evacuation; 30 Torr H_2 introduced prior to NO admission	10% Fe/Al_2O_3	1800, NO on Fe^{2+}; 1720, NO on Fe^0	Similar to reduced catalyst in absence of gas-phase H_2; overall NO band intensity is increased, especially Fe^0. Low concentration of oxidized NO species below 1600 cm^{-1}.
	10% Fe/1% K/Al_2O_3	1800, NO on Fe^{2+}; 1720, NO on Fe^0	Similar to reduced catalyst in absence of gas-phase H_2; overall NO band intensity increased, especially Fe^0; increasing intensity at 1220 cm^{-1}.
	10 Fe/1.5% K/Al_2O_3	1780, NO on Fe^{2+}; 1710, NO on Fe^0; 1300–1200 cm^{-1}, nitrite ions on alkali-perturbed sites	Similar to alkali-free catalyst in presence of gas-phase H_2 but with substantial shifting of bands to lower frequency; increasing band intensity in region 1220–1280 cm^{-1}.
	10% Fe/2% K/Al_2O_3	1770, NO on Fe^{2+}, 1700, NO on Fe^0; 1300–1200 cm^{-1}, nitrite ions on alkali-perturbed sites	Similar to 1.5% K case but with substantially lower intensity of NO bands and small shift of bands to lower frequencies; spectral intensity in the region 1200–1300 cm^{-1} increasing with increasing K and exceeds high-frequency bands.
H_2, 773K; evacuation	5% Fe/Al_2O_3	1800, NO on Fe^{2+}; 1720, NO on Fe^0	Substantially less Fe^0 compared with 10% Fe catalyst.

with regard to effect of alkali loading on catalyst properties. With the supported iron catalysts, alkali can deposit either on the support or on the iron particles, and the partitioning between these is not known. The alkali levels of 1.0, 1.5, and 2.0% are therefore of relative significance only. A commercially promoted iron Fischer–Tropsch catalyst containing 0.5–2.0% K_2O cannot be compared directly with the catalysts of the present study.

INFRARED RESULTS

All infrared spectra to be presented in this section were obtained by subtracting a background spectrum (catalyst at tempera-

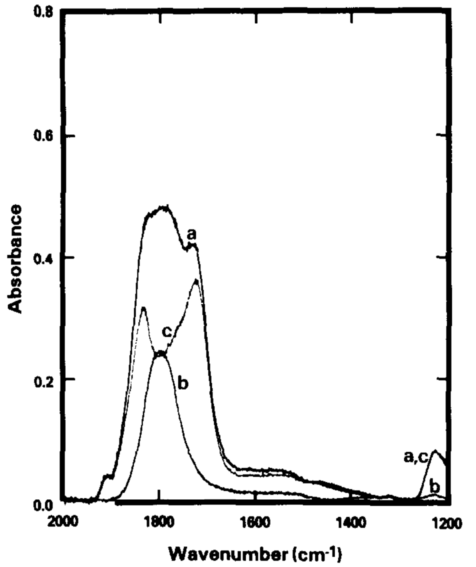

FIG. 2. Adsorption of NO on 10% Fe/Al_2O_3 reduced in H_2 at 773K. (a) Total adsorption with excess gas-phase NO; (b) after pumpout for 10 min to $<10^{-3}$ Torr; (c) difference spectrum, (a) − (b), representing weakly held NO.

ture in the absence of any chemisorption gases) from the total spectrum obtained following introduction of a gaseous component onto the catalyst surface. Because of the large number of spectra presented, the salient points are summarized in Table 1.

The infrared spectrum obtained when NO is chemisorbed on reduced, alkali-free 10% Fe/Al_2O_3 is shown in Fig. 2. The initial spectrum, obtained with gas-phase NO present (1–2 Torr), shows a pair of intense broad and overlapping bands centered near 1800 and 1720 cm^{-1}, along with less intense bands at 1920 and 1225 cm^{-1} (a). Upon evacuation of the cell to $<10^{-3}$ Torr, only a single band at 1800 cm^{-1} remains (b), which appears to be narrower than the original 1800-cm^{-1} band. This band will be termed "strongly held," as opposed to the "weakly held" bands which were removed during evacuation. The "weakly held" bands can be generated by subtraction and are also shown (c). At least four bands of this latter type can be distinguished, at 1920, 1840, 1720, and 1225 cm^{-1}; there is probably an additional fifth band which appears as a shoulder at 1760 cm^{-1}.

Assignments of the infrared bands at 1800 and 1720 cm^{-1} have been made by Bandow and co-workers (*11*), who reacted NO with iron vapor and trapped the products by matrix isolation techniques. They characterize the band at 1800 cm^{-1} as monomeric NO on Fe^{2+} sites, and a band at 1720 cm^{-1} as NO on fully reduced Fe^0. The Fe^{2+} sites were thought to be formed by oxidation of Fe^0 by NO. The species at 1720 cm^{-1} were removed more readily upon heating than the species at 1800 cm^{-1}. This is consistent with the present experiments, in which the 1720-cm^{-1} band was removed upon evacuation and is more weakly held than the species at 1800 cm^{-1}. In contrast to studies of NO chemisorbed on chromia/alumina (*12*), chromia/silica (*13*), or unsupported chromia (*14*), no evidence was found supporting formation of NO dimers in the matrix isolation experiments.

In the present experiments, the number of bands observed with alumina-supported iron are greater than that observed by matrix isolation. This indicates a greater surface complexity due to interaction between iron and the alumina. The assignment of the major bands at 1800 and 1720 cm^{-1} to Fe^{2+} and Fe^0 made by Bandow and co-workers (*11*) will be shown to be consistent with the present work. Assignment of the other weakly held bands cannot be definitively made at present, although approximate assignments are possible (*6*). The band position can be expected to indicate the oxidation level of the specific iron site, with increasing frequency of the NO band correlating with increasing oxidation state or electron deficiency of the site. Thus the small band at 1920 cm^{-1} could correspond to a NO^+ species formed on a highly oxidizing site (*15*). However, the possibility that the weakly held bands at 1840 and 1760 cm^{-1} are a NO dimer pair cannot be excluded (*6*).

The NO chemisorption spectrum shown by (a) in Fig. 2 indicates that the reduced

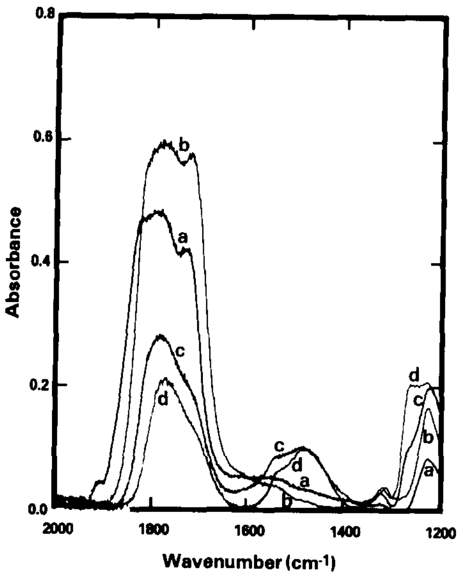

FIG. 3. Total NO adsorption (excess gas-phase NO) on 10% Fe/Al_2O_3 catalysts following reduction at 773K. (a) 0% K; (b) 1% K; (c) 1.5% K; (d) 2% K.

10% Fe/Al_2O_3 catalyst contains a substantial fraction of Fe^{2+} sites. This probably arises mostly from incomplete initial reduction of the catalyst surface, caused by strong interaction of iron sites with the alumina surface. Reoxidation of the surface by NO, as suggested by Bandow and co-workers (*11*), is less likely, since this results in formation of other (more oxidized) NO_x species (see below).

Figure 3 compares the total NO chemisorption spectra obtained (excess gas-phase NO) with the four supported iron catalysts described previously, following reduction at 773K. Qualitatively, the spectra obtained with the catalysts containing 0 and 1% K as K_2O are similar, as are the spectra from the catalysts containing 1.5 and 2.0% K. However, a substantial discontinuity in spectral pattern is seen in going from 1.0% K to 1.5% K. Comparing the 0 and 1% K catalysts, the addition of alkali results in an increase in total band intensity, and a shift of the major bands to lower wavenumber values. An additional difference to be noted is the disappearance of the band at 1920 cm^{-1} upon alkali addition. In comparing the 1.5% K and 2.05% K catalysts, a similar shift in the position of the bands near 1800 cm^{-1} is observed with increasing alkali content. However, with these latter two catalysts, the greater alkali loading results in a decrease in band intensity, suggesting a loss of surface sites for NO chemisorption. This loss in band intensity is partially compensated by increased band intensity below 1600 cm^{-1}. These bands are most consistent with oxidized NO species such as metal-bound nitro groups, nitrites, or nitrates (*6, 16–19*). Busca and Lorenzelli (*6*) have observed bands peaking at 1540 and 1220 cm^{-1} following nitric oxide chemisorption on α-Fe_2O_3, and have assigned these bands to the presence of nitrate species (NO_3^-), possibly bidentate. However, other assignments are possible.

After obtaining the spectra shown in Fig. 3 with each catalyst, the cell was evacuated, so that only strongly held species remained. The resulting spectra obtained with the four catalysts are shown in Fig. 4. Again, a discontinuity is observed in the

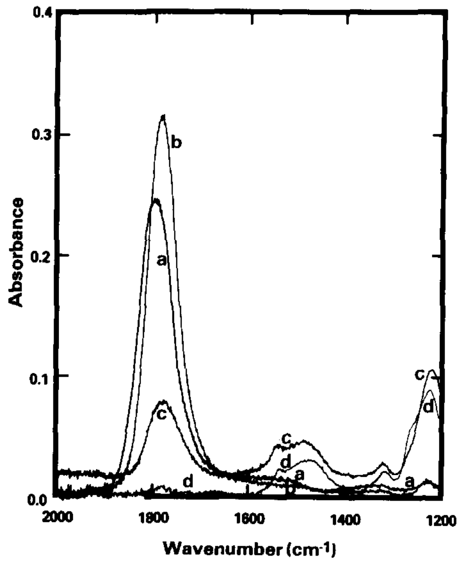

FIG. 4. Spectra of strongly held NO (10-min pumpout to $<10^{-3}$ Torr) for 10% Fe/Al_2O_3 catalysts following reduction at 773K. (a) 0% K; (b) 1% K; (c) 1.5% K; (d) 2% K.

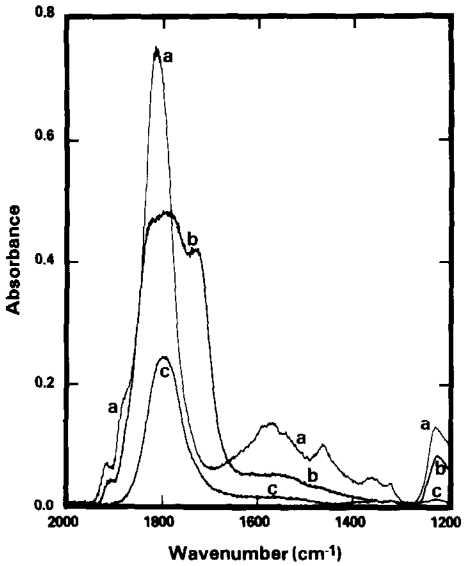

FIG. 5. Comparison of NO chemisorption on oxidized and reduced 10% Fe/Al_2O_3. (a) Total NO chemisorption on oxidized catalyst; (b) total NO chemisorption on reduced catalyst [same as Fig. 3(a)]; (c) strongly held NO on reduced catalyst.

spectral behavior between 1.0 and 1.5% K. Following an initial increase in NO intensity with the 1.0% K catalyst, the intensity of the strongly held NO bands decreases drastically with increasing alkali loading. On the iron catalyst containing 2.0% K, virtually no sites are present which can strongly chemisorb NO, although more oxidized NO species are observed.

The spectra from NO chemisorption on preoxidized and prereduced 10% Fe/Al_2O_3 are compared in Fig. 5. The oxidized catalyst was prepared by heating the catalyst in 3 cm of air at 773K for 30 min, followed by a 30-min evacuation at 773K. Intensity of the band near 1800 cm^{-1}, previously assigned to NO on Fe^{2+}, is substantially increased upon oxidation. The band near 1720 cm^{-1}, assigned to Fe^0, has disappeared. Appearance of additional bands in the region 1880–1920 cm^{-1}, and in the region below 1600 cm^{-1}, are consistent with production of electron-deficient and oxidizing sites, respectively. Following evacuation (not shown), all bands on the preoxidized catalyst remained except those in the region 1880–1920 cm^{-1}.

Figure 6 provides a comparison of total NO chemisorption (excess gas-phase NO) on the four catalysts following the oxidative pretreatment described above. The same discontinuity in spectral features is observed between 1.0 and 1.5% K loading as observed previously. A continuous shift in the peak maximum to lower wavenumber values is seen with increasing alkali loading for the major NO band near 1800 cm^{-1}. The NO bands observed in the region 1880–1920 cm^{-1} with 10% Fe/Al_2O_3 are not present with any of the alkali-containing catalysts, suggesting a removal or poisoning of these sites by K_2O. The low intensity of the bands obtained with 1.5 and 2.0% K catalysts suggests a catalyst surface which is poorly able to chemisorb NO in any form. It is interesting to note that the bands below 1600 cm^{-1} are no stronger with the preoxidized catalysts than with the prereduced catalysts. This suggests that these lower-frequency bands are caused more by the presence of alkali promoters than by excess surface oxygen derived from O_2.

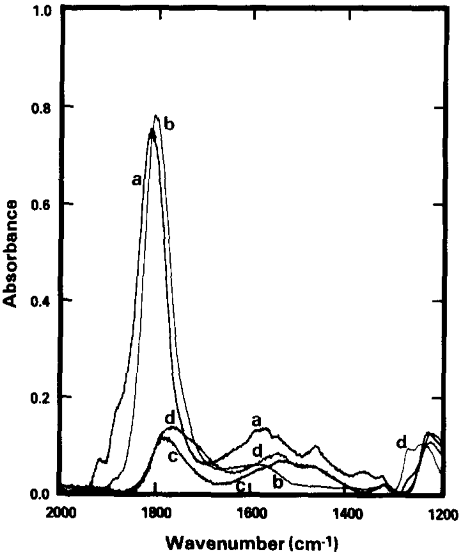

FIG. 6. NO chemisorption spectra on oxidized 10% Fe/Al_2O_3 catalysts, excess NO in gas phase. (a) 0% K; (b) 1% K; (c) 1.5% K; (d) 2% K.

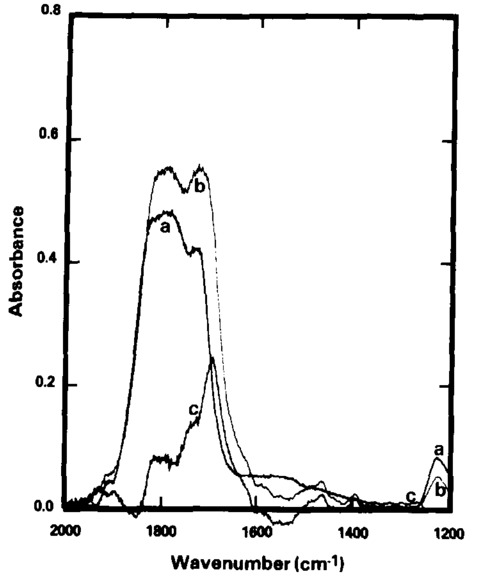

FIG. 7. Total NO chemisorption on 10% Fe/Al_2O_3, following (a) reduction at 773K, (b) introduction of 30 Torr H_2 gas prior to admission of NO to the sample. Trace (c) is difference spectrum, (b) − (a).

The oxidized catalysts characterized in Fig. 6 were then re-reduced in hydrogen at 773K. Following evacuation, a fresh charge of H_2 (30 Torr) was introduced prior to exposure of the catalyst surface to NO. The resulting spectrum is shown by (b) in Fig. 7 for 10% Fe/Al_2O_3. Compared with the spectrum obtained in the absence of excess gas-phase H_2 (a), the overall spectral intensity has increased. Especially pronounced is the relative increase in intensity of the band near 1720 cm^{-1}, previously assigned to NO chemisorbed on Fe^0. This is most clearly shown in the difference spectrum, (c) in Fig. 7. It appears that the presence of H_2 enhances sites more reduced than Fe^{2+}, especially Fe^0. This probably occurs by retarding dissociative chemisorption with resulting oxidation of the surface by NO, since H_2 at ambient temperatures should not provide further reduction for Fe/Al_2O_3 previously reduced at 773K. This effect was also observed in the matrix isolation experiments of Bandow and co-workers (*11*).

Spectra of NO chemisorbed on the four $Fe/(K)/Al_2O_3$ catalysts in the presence of gas-phase H_2 are shown in Fig. 8. In every case, the increase in spectral intensity near 1720 cm^{-1} is substantial. Especially pronounced is the increase in band intensity obtained with the 10% Fe/1.5% K/Al_2O_3 catalyst. The total NO chemisorption now appears to be as great or greater than the unalkalized 10% Fe catalyst. Although differing in total absorbance values, bands observed in the region 1600–1900 cm^{-1} with the four catalysts all have the same general features, i.e., a pair of bands nearly equal in intensity. A shift of these bands to lower wavenumbers with increasing alkali content of the catalyst can be observed. The effect of H_2 on the chemisorption of NO is reversible; following pumpout of gas-phase H_2 and NO and reintroduction of NO, spectra shown in Fig. 3 are again obtained.

It is interesting to compare the spectra obtained below 1600 cm^{-1} for NO chemisorbed on the reduced catalysts in the absence (Fig. 3) and presence (Fig. 8) of H_2. In the presence of H_2, a minimal absorption

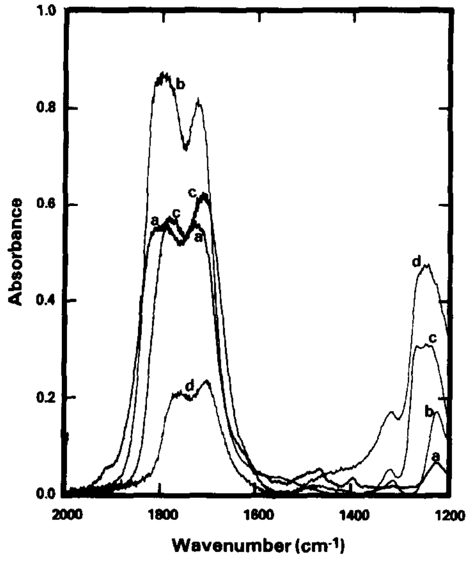

FIG. 8. Spectra of total NO chemisorption on 10% Fe/Al_2O_3 catalysts following admission of 30 Torr and subsequent admission of NO. (a) 0% K; (b) 1% K; (c) 1.5% K; (d) 2% K.

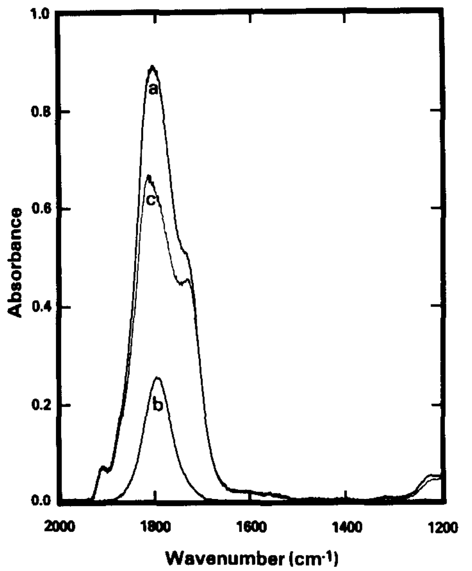

FIG. 9. NO chemisorption spectra on 5% Fe/Al_2O_3 catalyst following reduction in H_2 for 1 h at 773K. (a) Total NO chemisorption with excess gas-phase NO; (b) strongly held NO following pumpout for 10 min to $<10^{-3}$ Torr; (c) difference spectrum, (a) − (b), representing weakly held NO.

is observed in the spectral range 1500–1550 cm^{-1}, while significant band intensity is clearly evident in the H_2-free case. However, the bands in the range 1200–1250 cm^{-1} are much more prominent in the H_2-added case. This shows that the two sets of bands, both thought to be caused by oxidized NO species, derive from different sources. It is tempting to ascribe the bands between 1500 and 1550 cm^{-1} to species such as nitrite complexes ($M-NO_2$) produced by NO chemisorption on oxide sites initially generated by NO dissociation, since these bands increase as the 1720-cm^{-1} band (NO on reduced Fe) decreases. The bands in the region 1200–1250 cm^{-1}, present even when Fe^0 sites are present (see Fig. 8), are more consistent with a nitrite ion (NO_2^-) and appear to be strongly enhanced by the alkali oxide promoter under reducing conditions.

A final series of experiments were carried out to provide further data to support the assignment of the 1800- and 1720-cm^{-1} bands to NO on Fe^{2+} and Fe^0, respectively. Figure 9 shows the total, strongly held, and weakly held NO bands on 5% Fe/Al_2O_3. Low loadings of Fe on alumina (1–2%) have been shown to produce catalysts which have poor activity for Fischer–Tropsch catalysis (*20*), and this is thought to be due in large measure to the difficulty of reducing Fe^{2+} to catalytically active Fe^0. The 5% Fe/Al_2O_3 will catalyze the CO/H_2 reaction, but less effectively than 10% Fe/Al_2O_3 (*21*). Consistent with this, the spectra of the 5% Fe/Al_2O_3 catalyst indicate a greater proportion of sites assigned to Fe^{2+} and lesser amount of Fe^0 sites, relative to 10% Fe/Al_2O_3.

DISCUSSION

The addition of alkali to iron catalysts has been postulated to change selectivity for the Fischer–Tropsch reaction through modifying the properties of the surface toward CO and H_2 chemisorption. The specific mode of alkali action is not known, but general arguments have focused upon donation of electron density from basic K_2O to the iron sites. Upon chemisorption, it appears that the CO molecule withdraws electron density from the iron metal site, whereas chemisorbed hydrogen donates electron density (*4*). Increasing the electron density of the chemisorption site through alkali addition should then favor stronger chemisorption with CO and decreased strength of chemisorption with H_2. This is supported by measurements of CO and H_2 chemisorption on alkalized iron catalysts by Dry and co-workers, using calorimetric methods (*5*).

The effect of alkali on the chemisorption of CO on iron catalysts should be similar for chemisorption of NO. While chemisorption properties for the two diatomics differ, both have antibonding π^* orbitals which are capable of accepting electronic charge density from the metal chemisorption site. With an increase in this "back donation" comes stronger bonding between the metal site and the NO molecule, and a corresponding decrease in the strength of the NO bond. This latter phenomenon is what is measured by infrared spectroscopy. Therefore, changes in electron density of the iron chemisorption site should be reflected in the infrared frequency of chemisorbed NO, with increasing charge density resulting in shifts to lower frequencies (*6*).

The infrared measurements of NO chemisorbed on the four iron catalysts are consistent with a general progressive decrease in the NO stretching frequencies with increasing alkali loading. This is most clear with the NO band centered near 1800 cm^{-1} and assigned to NO on Fe^{2+}. This same effect can be seen with the catalytically more important Fe^0 sites, centered near 1720 cm^{-1}, but the correlation is not so clear except when gas-phase hydrogen is present (Fig. 8). This is due to the complex and changing nature of the catalyst surface with increasing loading of K_2O, which results in a drastic decrease in the NO band intensity in this region.

The infrared studies demonstrate the remarkable complexity of the iron/alumina catalyst surface. With the potassium oxide-free 10% Fe/Al_2O_3 catalyst, at least five separate bands can be distinguished and attributed to nondissociative NO chemisorption. This indicates that a variety of different local environments are present on the catalyst surface. All but one of these bands disappears following evacuation, indicating relatively weak chemisorption and lability of most of the chemisorbed NO. The most strongly held NO molecules appear to be coordinated to Fe^{2+} sites. The relatively large fraction of these sites may be due to reaction of the ferrous ions with the alumina surface to form iron-aluminates (*22*). Ionic iron in this form is not readily reducible with H_2. These aluminates are probably in substantial excess relative to their typical concentration on a reduced, unsupported iron Fischer–Tropsch catalyst.

Upon addition of potassium oxide to the iron catalyst, a variety of transformations are observed. At the lowest potassium loading (1% wt) the overall spectral features of the reduced catalyst are similar to those of the potassium-free catalyst, but the peak positions are shifted to lower frequencies. The most electron-deficient sites (NO bands near 1920 cm^{-1}) appear to be poisoned. As K_2O loading is increased, drastic changes in the shape and intensity of the NO bands are observed. Most notable is a decrease in overall spectral intensity, especially of the band ascribed to the Fe^0 sites. This Fe^0 band intensity correlated poorly with observed catalytic activity (see Microreactor Results).

In addition to the shift in position and the decreasing intensity of the bands ascribed to NO on Fe^0 and Fe^{2+}, the most striking change in the spectral features with alkali addition is the appearance of other nitrogen oxide species on the catalyst surface. There are two possible causes for this:

(i) Electron donation from alkali to the antibonding NO orbital via the Fe sites is, in some cases, sufficient to weaken and ultimately break the NO bond to form a surface nitride and surface oxide. The resulting surface oxide may combine with an additional NO molecule to form nitrite complexes or other bound NO_x species. Surface nitrides, oxides, and NO_x substantially cover the surface, retarding further NO chemisorption. Note that surface oxidation by dissociative NO chemisorption does not appear to generate more Fe^{2+} sites.

(ii) Sites perturbed by the K_2O promoter in a different manner from (i) result in formation of nitrite ions. These sites are more prominent under reducing conditions, especially with H_2 present in excess. Formation of both types of sites can account for the decreased amount of chemisorbed (unoxidized) NO which is observed as higher loadings of alkali promoter are added to the iron catalyst.

Iron catalysts are unique among the common Fischer–Tropsch catalysts, in that CO is thought to dissociate readily with iron to form a thermodynamically more favorable surface carbide and surface oxide at ambient temperatures (*23–25*). This is probably the major reason for the inability to observe by infrared spectroscopy chemisorbed CO on supported iron, although traces of oxygen have also been implicated (*8*). In view of the appearance of bands ascribable to Fe^0 when NO is chemisorbed onto the same catalyst, incomplete catalyst reduction cannot explain the lack of CO adsorption bands. Dissociative chemisorption appears to be somewhat less favorable for NO than for CO with iron, and requires potassium oxide promotion. However, even with K_2O, dissociation of NO can be retarded in the presence of H_2 (see Fig. 8). This suggests that a delicate balance exists between opposing forces either favoring or disfavoring dissociative chemisorption of NO on the iron catalyst surface.

It is likely that such a critical opposition of factors is also present on the surface of commercial iron Fischer–Tropsch catalysts during CO hydrogenation. In addition to competition between CO and H_2 for the adsorption sites, which is thought to determine olefin/paraffin ratios and hydrocarbon chain length (*4*), the mode of CO chemisorption may also be delicately balanced. Dissociative versus nondissociative chemisorption of CO may determine selectivity to hydrocarbons or oxygenated chemicals. Production of oxygenated chemicals with iron catalysts is known to be sensitive to such factors as reaction temperature, nature and extent of promoters, reactant partial pressure, and total pressure (*4*). It is clear that potassium oxide plays a key role in determining the selectivity balance in the Fischer–Tropsch synthesis with iron catalysts through alteration of its chemisorption properties.

REFERENCES

1. Raupp, G. B., and Delgass, W. N., *J. Catal.* **58**, 348 (1979); **58**, 361 (1979).

2. Amelse, J. A., Schwartz, L. H., and Butt, J. B., *J. Catal.* **72**, 95 (1981).

3. Anderson, R. B., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. III, pp. 119–140. Reinhold, New York, 1956.

4. Dry, M. E., *in* "Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. I. Springer-Verlag, New York, 1981.

5. Dry, M. E., Shingles, T., Boshoff, L. J., and Oosthuizen, G. J., *J. Catal.* **15**, 190 (1969); Dry, M. E., and Oosthuizen, G. J., *J. Catal.* **11**, 18 (1968).

6. Busca, G., and Lorenzelli, V., *J. Catal.* **72**, 303 (1981).

7. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **66**, 1664 (1962).

8. Heal, M. J., Leisegang, E. C., and Tarrington, R. G., *J. Catal.* **51**, 314 (1978).

9. Vannice, M. A., *Catal. Rev. Sci. Eng.* **14**, 153 (1976).

10. King, D. L., *J. Catal.* **51**, 386 (1978).

11. Bandow, H., Onishi, T., and Tamaru, K., *Chem. Lett.*, 83 (1978).

12. Peri, J. B., *J. Phys. Chem.* **78**, 588 (1974).

13. Kugler, E. L., Kokes, R. J., and Gryder, J. W., *J. Catal.* **36**, 142 (1975).

14. Kugler, E. L., and Gryder, J. W., *J. Catal.* **41**, 72 (1976).

15. Low, M. J. D., and Yang, R. T., *J. Catal.* **34**, 479 (1974).

16. Glazneva, G. V., Davydov, A. A., Sazonova, I. S., Shchekochikhin, Y. M., and Keier, N. P., *Kinet. Catal.* **19**(4), 997 (1978).

17. Blyholder, G., and Allen, M. C., *J. Phys. Chem.* **70**, 352 (1966).

18. Bellamy, L. J., "The Infrared Spectra of Complex Molecules." Wiley, New York, 1962.

19. Arai, H., *Ind. Eng. Chem. Prod. Res. Dev.* **19**, 507 (1980).

20. Dalmon, J. A., Dutartre, R., and Martin, G.-A., *C. R. Hebd. Seances Acad. Sci. Ser. C* **287**(16), 557 (1978).

21. King, D. L., unpublished results.

22. Anderson, J. R., "Structure of Metallic Catalysts." Academic Press, New York, 1975.

23. Yoshida, K., and Somorjai, G. A., *Surf. Sci.* **75**, 46 (1978).

24. Brundle, C. R., *IBM J. Res. Dev.* **22**, 235 (1978).

25. Barber, M., Vickerman, J., and Wohlstenholme, J., *Surf. Sci.* **68**, 130 (1977).