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The Use of Nitrous Oxide as a Surface Probe of Iron Catalysts for Fischer–Tropsch Synthesis

GERALD L. VOGLER,[1] XUAN-ZHEN JIANG,[2] J. A. DUMESIC,[3] AND R. J. MADON*

*Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706, and *Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, New Jersey 08801*

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Nitrous oxide was used as a probe of the surface of iron-based samples for Fischer–Tropsch synthesis. Identities of the bulk iron phases present were determined by Mössbauer spectroscopy. Both unpromoted and potassium-promoted iron samples were treated for 48 h in H_2/CO (1 : 1) at atmospheric pressure and temperatures ranging from 493 to 553 K. Wax produced during this treatment was washed from the samples by oxygen-free toluene at 373 K. After 1 h of evacuation at 650 K, the sample was dosed with N_2O at 298 K. This molecule oxidized the surface, accompanied by the formation of gaseous N_2. The unpromoted samples displayed two distinct reactivities with N_2O depending on the temperature of the H_2/CO treatment. Iron carbide was formed by treatment at 543 K, and about 10% of the surface area reacted with N_2O to form N_2. In contrast, about 75% of the surface of the unpromoted sample treated at 508 K for 48 h in H_2/CO reacted with N_2O. This sample was composed of about 90% magnetite and 10% iron carbide. The high reactivity toward N_2O of the sample treated in H_2/CO at 508 K was attributed to reduced iron species on the surface, while the low reactivity of the sample treated at 543 K was interpreted as being due to coverage of the surface by carbon deposits. Potassium-promoted iron treated in H_2/CO at temperatures below 515 K reacts with about the same amount of N_2O as the corresponding unpromoted catalyst. The promoted sample consisted of about equal amounts of magnetite and iron carbide, indicating that the potassium promoter increased the rate of iron carbide formation compared to the unpromoted sample. When the promoted iron sample was treated at 543 K, the extent of N_2O reaction was greater than that for the corresponding unpromoted sample. This sample consisted of iron carbide. The increase in the extent of N_2O reaction with the promoted compared to the unpromoted catalyst equaled the amount of potassium in the catalyst. Potassium cations do not react with nitrous oxide. Instead, the promoter enhances the extent of reaction of this probe molecule with iron.

INTRODUCTION

Potassium-promoted iron-based catalysts are used commercially in Fischer–Tropsch synthesis, i.e., the production of hydrocarbons from carbon monoxide and hydrogen. Anderson (*1*) and more recently Dry (*2*) have reviewed synthesis research on iron-based catalysts. In general, under reaction conditions the iron is usually present as magnetite (Fe_3O_4) and as one or more of the forms of iron carbide (e.g., Fe_5C_2, Fe_3C). Furthermore, a number of different forms of carbon may exist on the catalyst surface, e.g., amorphous carbon, graphitic carbon, and carbon associated with growing hydrocarbon chains. A description of the "active sites" on a given iron catalyst for Fischer–Tropsch synthesis thus requires knowledge about which phases of iron are present under the particular reaction conditions employed, and information about the amounts of oxygen and carbon associated with the surfaces of these phases. This is the subject of the present paper.

A flowing CO/H_2 gas mixture is strictly reducing at zero conversion for Fischer–Tropsch synthesis. Under these conditions,

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[1] Permanent address: 3M Company, 3M Center, St. Paul, Minn. 55144.

[2] Visiting scholar from Department of Chemistry, Zhejiang University, Hangzhou, Peoples' Republic of China.

[3] To whom correspondence should be addressed.

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iron carbides will be formed (*3–6*). However, during synthesis, water is formed as a primary product (*7*). At a sufficiently high H_2O/H_2 ratio in the gas phase, the surface of the iron catalyst may become oxidized (*8–11*). Indeed, at lower H_2O/H_2 ratios, oxygen species are still present on the iron surface. It has been proposed that partially oxidized iron surfaces are more active for Fischer–Tropsch synthesis than fully reduced surfaces (*10, 12*). It has also been proposed that the selectivity of CO_2, which is produced as a secondary product via water–gas shift, is enhanced by the presence of oxidized iron (*7*). Finally, the rate of the Boudouard reaction, and carbon deposition in general, is slower over oxidized iron surfaces than over reduced surfaces (*2, 8, 12*). Thus the amount of oxidized iron present seems to be important for the overall synthesis process.

Besides oxide formation or stabilization in iron-based Fischer–Tropsch catalysts, carbon deposition also plays an important role (*2, 13–17*). In general, carbon deposition becomes appreciable at temperatures above ca. 550 K. Some of this carbon can be hydrogenated to methane at moderate temperatures (e.g., 475 K), while other forms of carbon can be removed from the catalyst only at higher temperatures (e.g., above 625 K). The reactive form of carbon may be derived from carbidic carbon, and, this carbon becomes much less reactive upon transformation to graphitic carbon.

Addition of a potassium promoter to an iron catalyst for Fischer–Tropsch synthesis increases the heat of CO chemisorption and the rate of CO dissociation (*18, 19*). Accordingly, this increases the rate of carbon deposition and the rate of iron carbide formation (*2, 20, 21*).

A relationship may well exist between the rate of Fischer–Tropsch synthesis and the extent of carbon deposited on or incorporated into the iron catalyst. For example, Raupp and Delgass found that the conversion of CO during synthesis tracked the extent of iron carbide formation (*4*). Matsumoto (*22*) observed that the rate of Fischer–Tropsch synthesis initially increased as carbon was deposited on the catalyst, and then became constant at longer times. It is also apparent that extensive carbon deposition can lead to catalyst deactivation (*2*). These observations have been explained in terms of a competition for carbon in three general reactions (*23*). In particular, carbon may become incorporated into the catalyst as iron carbide, it may be hydrogenated to reactive species for Fischer–Tropsch synthesis, or it may react to form inactive (e.g., graphitic) carbon species which lead to catalyst deactivation.

It is apparent that an iron-based Fischer–Tropsch catalyst may contain carbon and oxygen both on the surface and in the bulk. It has been proposed (*7*) that the active site exists in the presence of both oxides and carbides, and its stability and performance are influenced by its proximity to certain phases. Catalyst characterization, therefore, involves both bulk and surface studies. Spectroscopic techniques, such as Mössbauer spectroscopy, are currently available for determination of the bulk phases of iron present under Fischer–Tropsch reaction conditions. Unfortunately, it is much more difficult to probe the surface of a high surface area (porous) Fischer–Tropsch catalyst. (In this respect it should be remembered that surface-sensitive techniques such as X-ray photoelectron spectroscopy monitor only the external surfaces of catalysts, i.e., they cannot be used to examine surfaces within the pores of a porous catalyst.) For this reason, the present study was undertaken to study the use of nitrous oxide as a surface probe of iron-based catalysts for Fischer–Tropsch synthesis. The basis for this technique has been developed previously for the study of copper catalysts (*24*). In short, N_2O reacts with reduced copper surfaces to give surface oxygen species and gaseous N_2. Analogously, it is suggested that N_2O may be used to probe the oxidation state of iron surfaces after exposure to various Fischer–Tropsch reaction conditions. To aid in the interpretation of such surface studies using nitrous oxide, the present study also employed Mössbauer spectroscopy to characterize the bulk phases of iron. In addition, both unpromoted and potassium-promoted samples have been investigated.

EXPERIMENTAL

Sample Preparation

Two samples were used primarily in this study. The first sample was unpromoted iron. This sample was chosen for study in order to eliminate the complicating effects from other promoters (textural or chemical) normally present in Fischer–Tropsch catalysts. For example, textural promoters (such as alumina) may cover a significant fraction of the iron surface, while chemical promoters (such as potassium) may alter the reactivity of iron. In addition, unsupported iron was chosen for study so that BET measurements could be used to determine the total iron surface area, thereby allowing the reactivity of the sample with respect to N_2O to be interpreted per iron surface area. In contrast, studies of N_2O reactivity with supported iron samples would have to be combined with chemisorption measurements to determine the iron surface area, and these latter measurements would require assumptions about how the chemisorptive properties of iron change as the chemical state of iron changes, e.g., between metal, carbide, oxide. The second sample investigated in the present study was iron promoted with potassium carbonate. This was studied to test whether the presence of the potassium promoter altered the chemical state or reactivity of iron.

The unpromoted sample was prepared by thermally decomposing $Fe(NO_3)_3 \cdot 9H_2O$ (ACS grade from Matheson, Coleman, and Bell Manufacturing Chemist). The ferric nitrate was heated and stirred until it first turned to a liquid and then it turned to a rust-colored powder. The powder was placed in an oven at 380 K for 12 h and subsequently ground to 65/200 mesh size.

The promoted sample was prepared by coprecipitation of $FeCl_2 \cdot 4H_2O$ (Analytical grade from Mallinckrodt Chemical Works) and $FeCl_3 \cdot 6H_2O$ (ACS from Matheson, Coleman, and Bell) using Na_2CO_3 (Technical grade from Mallinckrodt Chemical Works) similar to the procedure described by Jacobs (*25*). Potassium was then added to the sample via impregnation of K_2CO_3 (Analytical Reagent grade from Mallinckrodt Chemical Works). The sample was dried at 380 K overnight for 12 h and subsequently ground to 65/200 mesh size. The potassium loading on this sample was 0.19 wt%, as determined by chemical analysis (Galbraith Laboratories).

For comparison with the behavior of the above samples, a sample of pure magnetite and a sample of potassium carbonate impregnated on silica were also prepared. These will be described in the results section of this paper.

H_2/CO Treatment System

The above samples were pretreated in H_2/CO prior to surface oxidation studies using N_2O. As will be shown later, the iron was present as iron oxide and iron carbide after these treatments, with surface areas between 10 and 40 m^2/g. Samples were not studied after reduction to metallic iron by pure hydrogen, due to the loss of surface area which accompanies this treatment.

Hydrogen (National Cylinder Gases) was purified by passage through a Deoxo unit followed by a copper-turnings trap at 570 K and an activated 13× molecular sieve trap submerged in a dry ice–acetone bath (195 K). Carbon monoxide (C.P. grade from Matheson) was purified by passage through a heated U-tube, a copper-turnings trap at 570 K, and a molecular sieve trap at room temperature. The U-tube was at 570 K to decompose any metal carbonyls that may be present in the gaseous CO. Individual gas flow rates were monitored by LoFlo rotameters (S. K. Instruments) which were calibrated with a bubble flow meter that was fed from a water saturator. Calibrated flow rates were adjusted to atmospheric pressure and 273 K. The gas streams were mixed after the purification trains and passed through the pyrex cell which contained the sample.

Toluene Wash System

The reaction of CO and H_2 on an iron catalyst produces high-molecular-weight hydrocarbons which are liquids at 500 K and solids at room temperature. It was desirable to remove these hydrocarbons from the surface and pores of the catalyst prior to studies of N_2O reactions with the sample.

McCartney *et al.* (*11*) and Pichler and Merkel (*26*) have described techniques for extracting hydrocarbons from catalysts using toluene in modified Soxhlet extractors. These procedures were modified such that the sample could be washed in the same cell in which reaction with N_2O was subsequently studied. This avoided exposure of the sample to air, as described in detail elsewhere (*27*). In short, an extraction funnel was modified such that it could be connected directly to the sample cell. The funnel was filled with toluene (certified 99 mol% pure from Fisher Scientific Co.) and sparged with purified helium for 10–20 h to remove dissolved oxygen. Helium (Badger Welding Supplies) was purified by passage through a copper-turnings trap at 570 K followed by an activated 13× molecular sieve trap submerged in liquid nitrogen (77 K).

After the sample was treated in H_2/CO, the cell was quenched to room temperature within 15 min. The gases in the cell were evacuated to 10^{-2} Pa. A boiling water bath (373 K) was placed around the cell, and toluene was allowed to flow into the cell until the sample was covered. The toluene was left in the cell for 3 min after which it was evacuated from the cell and collected in receiving vessels which were at 77 K and under 10^{-2} Pa vacuum. It generally required three wash cycles to remove all of the wax. The toluene in the last wash cycle was always clear of the yellow wax color. The sample was then submitted to a standard vacuum treatment of 1 h at 650 K in a vacuum of 10^{-4} Pa. This treatment, suggested by Lund *et al.* (*28*) for iron oxides, gives reproducible results for surface titrations by NO.

The effectiveness of this toluene wash method was analyzed using Fourier transform infrared spectroscopy. The C–H alkane vibrations were monitored in the 2850 to 3000 cm^{-1} range. For this purpose it was necessary to wash the catalyst sample with a solvent which did not contain an alkyl group; benzene was chosen. Four samples were prepared in separate vials for FTIR analysis in the following manner:

(1) About 100 mg of used catalyst was mixed with 0.80 ml of benzene. This sample was previously washed with 373 K toluene and treated under vacuum at 650 K for 1 h.

(2) About 100 mg of used catalyst was mixed with 0.80 ml of benzene. This sample was previously treated under vacuum at 650 K for 1 h.

(3) About 18 mg of wax, formed during one of the runs, was mixed with 2.40 ml of benzene.

(4) Pure benzene was used for a blank. Each vial was heated briefly until the benzene began to boil.

The spectra of the four samples are shown in Fig. 1. The sample with the highest absorbance in the 2850–3000 cm^{-1} range, thus the highest concentration of wax, was the wax/benzene solution. Second highest on the absorbance scale was the benzene wash for the catalyst which had been treated only under vacuum at high temperature. The benzene blank and the benzene wash for the toluene-washed catalyst gave essentially identical spectra. Hence the toluene wash is effective and essential to remove the wax from the catalyst.

Surface Oxidation Method

After the sample had been washed with toluene at 373 K and was treated in vacuum

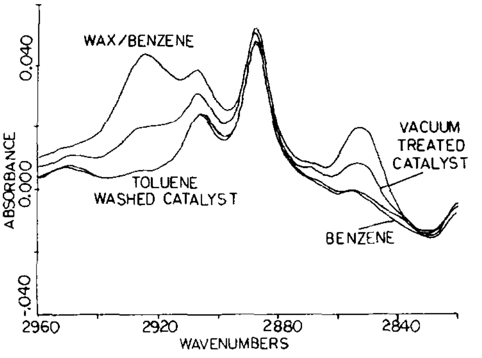

FIG. 1. Infrared spectra of toluene-washed and unwashed samples. Spectra collected in benzene and compared to spectra with different amounts of wax in benzene.

for 1 h at 650 K, it was cooled to room temperature. Nitrous oxide was then dosed into the cell to an initial pressure of about 37 kPa (280 Torr). Room temperature was chosen for these studies since the reaction of N_2O with the samples is slower at lower temperatures, while N_2O may oxidize bulk iron at significantly higher temperatures. In separate experiments we have shown that approximately 4 monolayers of metallic iron are oxidized upon prolonged exposure to N_2O at room temperature. The N_2O (CP grade, 99.0% pure, from Matheson) was purified by freezing the N_2O in liquid nitrogen (77 K) followed by vacuum pumping. This freeze–pump–thaw cycle was repeated until consecutive freezings yielded zero pressure readings.

Nitrous oxide reacts with reduced iron near the surface to produce oxidized iron and a gas phase nitrogen molecule, as shown schematically below:

$$N_2O_{(g)} + (Fe)_{(surface)} \rightarrow N_{2(g)} + (FeO)_{(surface)} \quad (1)$$

where (Fe) and (FeO) represent reduced and oxidized iron species, respectively. During this reaction the total pressure remains constant, indicating that N_2O and N_2 do not adsorb to significant extent on the iron surface (*27*). Mass spectra of the product gases after exposure of N_2O to the iron samples contain peaks due only to N_2 and N_2O. Thus, to determine the extent of iron oxidation by N_2O, it is sufficient to measure the amount of gaseous N_2 formed. This can be accomplished by freezing the N_2O from the gas mixture at liquid nitrogen temperatures (77 K). At this temperature, the vapor pressure of N_2O is less than 10^{-4} kPa.

It should be noted that the possible complication of the presence of CO and CO_2 in the gas phase during these studies involving N_2 and N_2O can be neglected. In particular, the vacuum pretreatment of the sample prior to exposure to N_2O is sufficient to remove both CO (e.g., *29*) and CO_2 (*30*) from the iron surface. As mentioned above, experiments showed that the amount of N_2 or N_2O which adsorbs on the sample can be neglected, since the total gas pressure does not decrease (except due to dead-volume effects) after each dose of N_2O into the sample cell. Indeed, while it may have been anticipated that nitrogen may adsorb on reduced iron, it is also true that the rate of dissociative nitrogen adsorption is very slow (e.g., *31*).

The reaction of N_2O with the iron samples of this study was studied using the glass apparatus shown schematically in Fig. 2. This apparatus is equipped with a precision pressure gage (Texas Instruments) for measurement of total pressures before freezing of N_2O, and determination of N_2

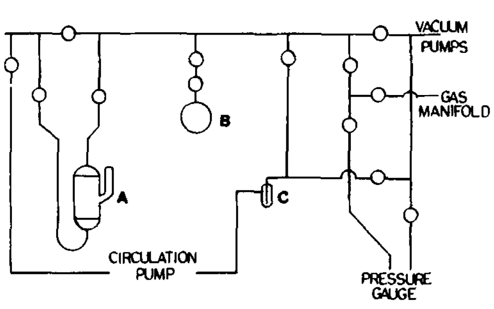

FIG. 2. Gas handling system used in studies of nitrous oxide reaction with iron samples and used for BET measurements. (A) Sample cell; (B) removable glass bulb for mass spectroscopy analysis; (C) cold trap; ○ denotes stopcocks.

pressures after freezing of N_2O. These pressures were used to calculate the quantities of N_2O and N_2 in the gas phase. This involved previous calibration of all of the appropriate volumes of the apparatus.

To expedite the freezing process used to determine the nitrogen partial pressure, a dual action reciprocating pump was developed to circulate the gases through the manifold and the cell. The design of this pump has been described elsewhere (*27*). After the sample had been equilibrated in N_2O for a given period of time (as will be described later), the gas was mixed by circulation through the system and the cell. The bypass stopcock, between the cell inlet and outlet, was closed during this process to force gas through the cell. After approximately 10 min of circulating, the pump was turned off, the bypass stopcock was opened, and the stopcocks for the cell were closed. Liquid nitrogen was then placed around the cold trap to freeze the N_2O. The cell was isolated during this process so that the pressure and the gas phase composition over the catalyst would not change during the N_2 analysis. The gas was then circulated through the cold trap for about 1.5 h, during which time the pressure in the system decreased to a constant value. This pressure was used to calculate the amount of N_2 in the system. After the final pressure was recorded, the N_2O was thawed and the cell was opened to the system to continue the surface oxidation in N_2O.

BET Surface Area Measurements

BET surface areas were determined by the static volumetric method. The glass apparatus used for the surface oxidation studies in N_2O was also employed for these BET surface area measurements. To reduce the dead volume during these measurements, the pump was isolated from the system. N_2 (Badger Tube and Welding) was purified by passage through a copper-turnings trap at 520 K followed by an activated 13× molecular sieve trap submerged in liquid nitrogen.

Mössbauer Spectroscopy

Mössbauer spectra were collected using an Austin Science Associates, Inc., model S-600 spectrometer. The details of this spectrometer have been reported elsewhere (*32*). In short, all spectra were collected in the constant acceleration Doppler velocity mode. Data were transmitted to a PDP 11/55 computer for storage and subsequent analysis using the program MFIT (*33*). A 6.35-μm metallic iron foil was used to calibrate the Doppler velocity. Isomer shifts are reported relative to this standard absorber at room temperature. Mössbauer spectra were collected for each sample following surface oxidation studies in N_2O. The samples were passivated before exposure to air and collection of the Mössbauer spectra. This was accomplished by first filling the catalyst cell with He to atmospheric pressure, and then allowing air to diffuse into the catalyst cell at room temperature over a period of several hours.

The primary objective of the Mössbauer spectroscopy studies was to determine the relative amounts of iron oxide (magnetite) and iron carbide present in the samples after various treatments. The Mössbauer spectrum of magnetite is a 12-peak pattern due to two partially overlapping sextuplets. The separation between the outermost peaks of these sextuplets is about 15 mm/s. The Mössbauer spectra of iron carbides are more complex than that of magnetite. For example, the spectrum of χ-carbide consists of three partially overlapping sextuplets. Of importance, however, is the fact that the separation between the outermost peaks of the various iron carbides is about 7 mm/s. Thus, it is relatively straightforward to determine the spectral area of magnetite relative to that of iron carbide. It is much more difficult, however, to identify the precise nature of the iron carbide phases from Mössbauer spectroscopy, especially in the presence of magnetite. It will be seen in the results section that the Mössbauer spectra of the present study can be adequately fit

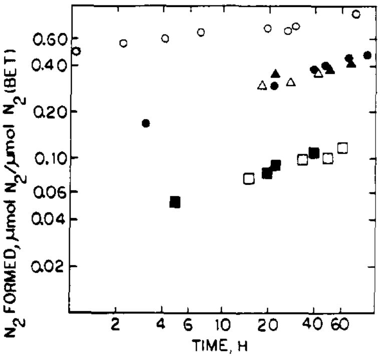

FIG. 3. Amount of N_2 formed during reaction of N_2O with unpromoted iron samples. (○) Treated in H_2/CO at 508 K; (□) treated in H_2/CO at 543 K; (△) treated in CO/CO_2 at 650 K. Filled and open symbols refer to unwashed and toluene-washed samples, respectively.

by combinations of contributions from magnetite and χ-carbide. In view of the above remarks, though, this does not exclude the possibility that smaller amounts of other carbides may also be present.

Due to the presence of at least 30 peaks in spectra containing magnetite and iron carbide, the computer fitting was initially carried out using physical constraints, as described in detail elsewhere (*27*). In short, the positions of these 30 peaks were constrained to be equal to those known values for the individual phases reported in the literature. The computer was allowed to vary the widths and intensities of these peaks. Finally, the constraints on the peak positions were released, and the computer was allowed to find the best fit of the spectrum using 5-sextuplets. For each sextuplet, the widths and areas of the two peaks in each of the following pairs were constrained to be equal: 1 and 6, 2 and 5, 3 and 4, numbering peaks from negative toward positive velocities. In addition, the relative positions of these six peaks were constrained to be consistent with the known nuclear magnetic moments of iron.

RESULTS

Unpromoted Iron Samples

Unpromoted iron samples were treated for 48 h at atmospheric pressure, in a feedstream of $H_2/CO = 1$ gas, at either 508 or 543 K, at a space velocity of 3.0×10^4 ml h^{-1} g^{-1} (STP). At the end of the 48 h treatment, the reactor cell was cooled to room temperature within 15 min. For half of the experiments the samples were washed with toluene, while for the other half this wash was omitted.

When the unpromoted sample was treated at 508 K, the subsequent extent of nitrogen formation due to the nitrous oxide surface reaction was greater than that measured after the catalyst was treated at 543 K, as shown in Fig. 3. For the catalyst treated at 508 K, the degree to which the surface was oxidized by N_2O also depended on whether the catalyst was washed with toluene, i.e., the toluene wash increased the extent of N_2 formation per BET surface area. In contrast, the toluene wash had no effect on the reactivity of the sample after treatment at 543 K. A listing of the BET surface areas for all of the unpromoted samples appears in Table 1. It can be seen that the surface area was not altered by the toluene wash and the surface area was larger after treatment at 543 K compared to the samples treated at 508 K.

Following the nitrous oxide reaction study and BET surface area determination, a room temperature Mössbauer spectrum of the sample treated at 508 K was collected

TABLE 1

BET Surface Areas for Unpromoted Iron Samples

Catalyst treatment[a]	Treatment temp. K	Washed with toluene	BET area (m^2/g precursor)
1	508	yes	21.2
1	508	yes	19.6
1	508	no	19.6
1	543	yes	33.6
1	543	no	33.7
2	653	yes	11.3
2	673	no	10.2

[a] (1) $CO/H_2 = 1$ for 48 h. (2) $CO_2/CO = 5.7$ for ca. 6 h.

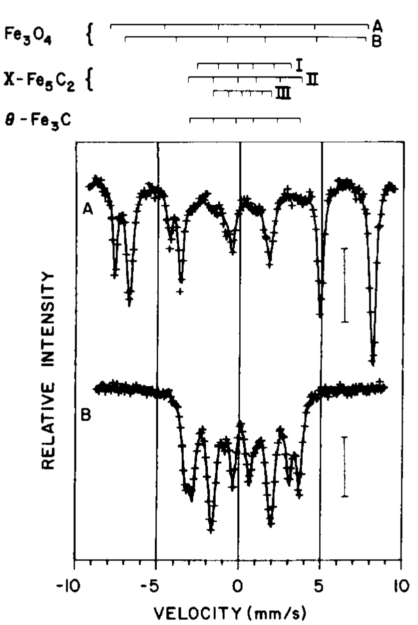

FIG. 4. Room temperature Mössbauer spectra of unpromoted iron samples. (A) Treated in H_2/CO (1 : 1) at 508 K; (B) treated in H_2/CO (1 : 1) at 543 K. Vertical bars correspond to a 0.5% change in transmission.

and is shown in Fig. 4A. The solid line is the computer-fitted line and the stick diagram above the spectrum designates the positions of the individual peaks for each of the five sextuplets. The major portion of the area of the spectrum is due to the two sextuplets with the largest splittings, designated as A and B. The hyperfine fields and isomer shifts for these two sextuplets, which are tabulated in Table 2, agree with the literature values for magnetite (*34*). The Mössbauer parameters for the other three sextuplets, which are also presented in Table 2, agree with the literature values for χ-carbide (*35*, *36*). Assuming equal recoilless fractions for both magnetite and carbide, it can be estimated that about 90% of the iron was present as magnetite in this sample.

A room temperature Mössbauer spectrum of the sample treated in H_2/CO at 543 K appears in Fig. 4B. This spectrum was fit with three sets of sextuplets. The isomer shifts and hyperfine fields for these sextu-

TABLE 2

Computer-Fit Mössbauer Parameters for Unpromoted Samples of Fig. 4

Sample	Compound	Site[a]	Hyperfine field (kOe)	Isomer shift (mm/s)	Relative site population[b]	Carbide (%)
Sample of Fig. 4A	Fe_3O_4	A	492	0.28	1	10%
		B	460	0.65	2	
	χ-Fe_5C_2	I	181	0.31	1.2	
		II	218	0.39	1.8	
		III	119	0.27	1	
Sample of Fig. 4B	χ-Fe_5C_2	I	182	0.13	1.7	100%
		II	216	0.16	2	
		III	109	0.16	1	
Literature values[c]	Fe_3O_4	A[b]	491	0.258	1	
		B[b]	461	0.461	2	
	χ-Fe_5C_2	I[c]	184	0.30	2	
		II[c]	222	0.35	2	
		III[c]	110	0.30	1	

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[a] A and B refer to the tetrahedral and octahedral sites, respectively, in the close-packed oxide structure; I, II, III designate the three different lattice sites of χ-Fe_5C_2.

[b] Relative population of each lattice site for that compound.

[c] Parameters for Fe_3O_4 from ref. (*34*); parameters for iron carbide from refs. (*35*, *36*).

plets agree with the literature values for χ-carbide. No iron oxide peaks were apparent in this spectrum. The Mössbauer parameters for this spectrum are listed in Table 2.

In a separate run, one sample was treated for 48 h at atmospheric pressure and 543 K in a H_2/CO (1 : 1) gas mixture saturated with water vapor at room temperature (i.e., 2.7% H_2O). The presence of this H_2O in the H_2/CO feedstream had a significant effect on the state of the catalyst. When no H_2O was present in the H_2/CO feed, as described above, the 543 K treatment resulted in the production of iron carbide. However, when the H_2/CO feed was saturated with H_2O, the sample gave a Mössbauer spectrum which contained only magnetite. The hyperfine fields of 489 and 461 kOe and the isomer shifts of 0.27 and 0.67 mm/s agree with the literature values listed in Table 2.

Magnetite Samples

It was shown above that the extent of N_2O reaction with unpromoted iron treated at 508 K was increased by washing the sample with toluene. This sample consisted primarily of magnetite. One possible effect of the toluene wash might be to reduce the magnetite surface, instead of merely removing wax from the sample. To test this possibility, experiments were conducted on magnetite samples which had not been exposed to H_2/CO gas mixtures, i.e., which did not contain wax.

Unsupported Fe_3O_4 was precipitated from a 2 : 1 molar solution of ferric and ferrous ammonium sulfate salts by the addition of ammonium hydroxide. This procedure was adapted from work done by Lund *et al.* (*28*). The precipitate was washed with distilled H_2O and then dried in an oven at 380 K under flowing N_2. The dried sample was ground to 200/65 mesh size. The sample was subsequently treated with 15% CO in CO_2 for 8 h at 670 K. This treatment has been shown by Mössbauer spectroscopy to convert all of the iron to magnetite. Next, the sample was evacuated for 1 h at 650 K. Following cooling to room temperature, the sample was dosed with N_2O to an initial pressure of ca. 37 kPa (280 Torr). The extent of N_2 formation was determined as well as the BET surface area. The sample was then treated in CO/CO_2 at 650 K for 5 h to regenerate the initial magnetite state. This was followed by toluene washing at 373 K, evacuation at 650 K, and dosing the sample with N_2O at room temperature. After the extent of N_2 formation was determined, the BET surface area was measured. It can be seen in Fig. 3 that the toluene wash does not affect the N_2O surface reaction on pure magnetite.

Silica Supported Potassium Carbonate

Potassium carbonate (Analytical Reagent grade from Mallinckrodt Chemical Works) was impregnated on SiO_2 (Cab-O-Sil fumed silica, grade MS-75 from Cabot Corp.) by incipient wetness. Elemental analysis of this sample (Galbraith Laboratories) indicated a potassium loading of 3.4 wt%. The sample was treated in $H_2/CO = 1$ for 48 h at 533 K. After evacuation at 650 K for 1 h, the cell was cooled to room temperature and dosed with N_2O to an initial pressure of ca. 37 kPa (280 Torr). Chemical analysis of this treated sample showed that the potassium loading had remained 3.4 wt%. N_2O reacted slowly and to a very low extent with the K_2CO_3/SiO_2 sample. After 85 h, 6.1 μmol of N_2 were produced from N_2O per gram of sample, compared to the 880 μmol of potassium which were contained in the sample.

Potassium-Promoted Iron Samples

The iron sample promoted with potassium carbonate was treated in $H_2/CO = 1$ for 48 h under atmospheric pressure at either 493 or at 543 K using a space velocity of 3.0×10^4 ml g^{-1} h^{-1}. It should be noted that under these conditions the potassium promoter is probably associated with oxygen and is not in the metallic state. Thus, the term "potassium-promoted" used in this paper should be interpreted in this con-

TABLE 3

BET Surface Areas for Potassium-Promoted Samples

Sample	Highest treatment temperature, K	Washed with toluene	BET surface area (m^2/g)
Sample of Fig. 6B	493	Yes	35.7
Sample of Fig. 6A	543	Yes	42.9
FeK-1	513	Yes	28.9
FeK-2	553	Yes	34.7
FeK-3	553	Yes	37.2
FeK-4	543	Yes	40.8

text. The sample was then washed with toluene at 373 K, cleaned by evacuation (10^{-4} Pa) for 1 h at 650 K, and dosed with N_2O at room temperature to an initial pressure of about 37 kPa (280 Torr). The BET surface area was measured following the N_2O reaction study (see Table 3). A Mössbauer spectrum of the sample was then collected.

The results of the N_2O reaction studies over the promoted samples agreed qualitatively with the results from the unpromoted samples. When the samples were treated at the lower synthesis temperatures, more N_2 was produced from N_2O than for the samples treated at the high temperature. The results for both the promoted and the unpromoted samples are shown in Fig. 5. The potassium-promoted sample which was treated at 543 K shows an enhancement in the extent of N_2O reaction compared to the unpromoted sample. In contrast, for the samples treated at the lower temperature, the promoted sample showed about the same extent of N_2O reaction.

The Mössbauer spectrum of the promoted iron sample treated at 543 K is shown in Fig. 6A. As for the unpromoted sample, the spectrum was fit adequately by the 18-peak pattern of χ-Fe_5C_2. A summary of the Mössbauer parameters appears in Table 4.

The Mössbauer spectrum for the potassium-promoted sample treated at 493 K in

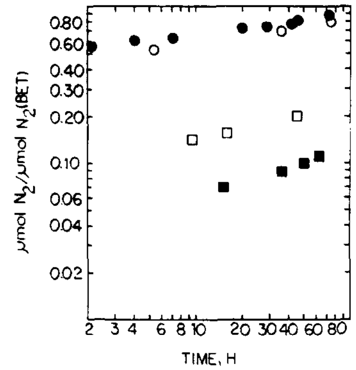

FIG. 5. Amount of N_2 formed during reaction of N_2O with unpromoted versus potassium-promoted iron samples washed with toluene. (●) Unpromoted sample treated in H_2/CO at 508 K; (○) promoted sample treated in H_2/CO at 493 K; (■) unpromoted sample treated in H_2/CO at 543 K; (□) promoted sample treated in H_2/CO at 543 K.

H_2/CO differed in the amount of Fe_3O_4 present, compared to the unpromoted sample treated at the similar temperature of 508 K. Assuming equal recoilless fractions for iron carbide and for Fe_3O_4, the unpromoted sample contained about 90% Fe_3O_4 whereas the potassium-promoted sample, shown in Fig. 6B, contained about 50% Fe_3O_4. A summary of the Mössbauer parameters for

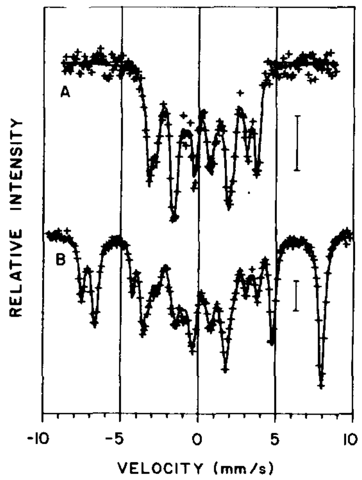

FIG. 6. Room temperature Mössbauer spectra of potassium-promoted iron samples. (A) Treated in H_2/CO (1 : 1) at 543 K; (B) treated in H_2/CO (1 : 1) at 493 K. Vertical bars correspond to a 0.2% change in transmission.

TABLE 4

Computer-Fit Mössbauer Parameters for Potassium-Promoted Samples of Fig. 6

Sample	Compound	Site[a]	Hyperfine field (kOe)	Isomer shift (mm/s)	Relative site population[b]	Carbide (%)
Sample of Fig. 6A	χ-Fe_5C_2	I	182	0.17	1.7	100%
		II	218	0.24	1.4	
		III	113	0.19	1.0	
Sample of Fig. 6B	Fe_3O_4	A	483	0.21	1.0	48%
		B	456	0.63	1.7	
	χ-Fe_5C_2	I	178	0.21	2.0	
		II	221	0.28	2.1	
		III	107	0.44	1.0	

[a] A and B refer to the tetrahedral and octahedral sites, respectively, in the close-packed oxide structure; I, II, III designate the three different lattice sites of χ-Fe_5C_2.

[b] Relative population of each lattice site for that compound.

the sample treated at this low reaction temperature appears in Table 4. It is interesting that these two samples containing different relative amounts of magnetite and iron carbide show about the same reactivity with N_2O (see Fig. 5). This will be discussed later.

In a separate series of experiments, the potassium-promoted sample was treated for various lengths of times at different temperatures. All of these runs employed a space velocity of 6.3×10^3 ml h^{-1} g^{-1} at atmospheric pressure and a H_2/CO ratio of 1.5. At the end of each run, the sample was cooled to room temperature (in about 15 min), washed with toluene at 373 K, evacuated at 650 K for 1 h, and dosed with N_2O at room temperature to an initial pressure of 37 kPa (280 Torr). The extent of surface oxidation by N_2O was then determined. Subsequent to this, the BET surface area was measured and a Mössbauer spectrum was collected.

In the first run, FeK-1, the sample was treated for about 60 h at temperatures between 490 and 510 K. The extent of N_2O reaction with FeK-1 was only slightly lower than that for the above samples treated at low temperatures: below 515 K. This is shown in Fig. 7. The Mössbauer spectrum of FeK-1 contains 96% χ-Fe_5C_2 and only about 4% Fe_3O_4. As described above, the previous low temperature runs contained about 90% Fe_3O_4 for the unpromoted sample and 50% Fe_3O_4 for the promoted sample. It appears again that the surface reactivity toward N_2O is independent of the relative amounts of bulk magnetite and iron carbide, as long as both of these bulk phases are present.

In Runs FeK-2, FeK-3, and FeK-4, the temperature of Fischer–Tropsch synthesis was raised above 540 K during the course of the experiments. The time of treatment

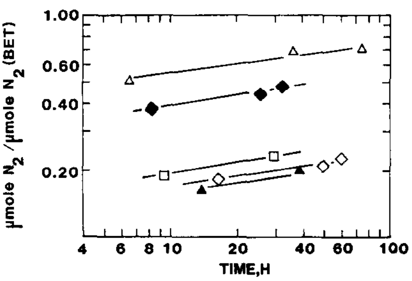

FIG. 7. Amount of N_2 formed during reaction of N_2O with potassium-promoted iron samples treated for various lengths of times at different temperatures and washed with toluene: (△) K-promoted iron treated at 493 K. FeK series of runs: (◆) FeK-1; (□) FeK-2; (◇) FeK-3; (▲) FeK-4.

at temperatures between 540 and 550 K was equal to 10, 20, and 60 h in these three runs, respectively. Further details of the temperature histories of these treatments can be found elsewhere (*27*). The BET surface areas of the samples from Runs FeK-1 through FeK-4 are given in Table 3.

The samples of Runs FeK-2, FeK-3, and FeK-4 produced similar amounts of N_2 upon exposure to N_2O at room temperature. This is shown in Fig. 7. These samples also have Mössbauer spectra that are essentially identical, and are characteristic of χ-Fe_5C_2. The general result of these runs is that all of these samples which show only iron carbide in their Mössbauer spectra also exhibit low reactivities with N_2O.

DISCUSSION

Unpromoted Iron Samples

The results of this study have demonstrated that surface oxidation by N_2O can differentiate samples which have been treated under different conditions. Mössbauer spectroscopy has complemented these N_2O studies by providing information about the identity of the bulk iron phases. The results of Mössbauer spectroscopy will be discussed before the results of the N_2O surface oxidation studies. After a 48 h treatment at 508 K in H_2/CO, the composition of the sample was identified by Mössbauer spectroscopy to be ca. 90% Fe_3O_4 and the remainder to be iron carbide. However, the same precursor yielded 100% iron carbide when the H_2/CO reaction temperature was increased to 543 K. In contrast, when the sample was treated at 543 K in a H_2/CO gas mixture containing about 2.7% water, the sample was observed to be essentially pure magnetite.

The pronounced effect of water vapor in determining the bulk state of iron in the present study is in agreement with previous studies of iron Fischer–Tropsch catalysts (e.g., *1*, *2*). During Fischer–Tropsch synthesis, an iron catalyst is in an atmosphere of H_2O, CO_2 as well as the Fischer–Tropsch reactants CO and H_2. In general, the phase of the catalyst depends on the ratios of H_2O/H_2 and CO_2/CO, although the former ratio is probably the more important of the two. According to Bohlbro (*8*) a water content greater than 1.1% in a H_2 feedstream is necessary for Fe_3O_4 to be thermodynamically stable at 500 K. Furthermore, CO_2 concentrations in CO must be greater than 55% for Fe_3O_4 to be stable in relation to metallic Fe. Over an iron catalyst, H_2O is a direct product of Fischer–Tropsch synthesis (e.g., *7*).

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \quad (2)$$

Carbon dioxide is a secondary product, produced by the water–gas shift reaction:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (3)$$

According to the above thermodynamic results, CO conversion during Fischer–Tropsch synthesis has to be greater than about 1% for Fe_3O_4 to be stable according to the H_2O/H_2 ratio. A CO conversion of at least 35% for the Fischer–Tropsch reaction and extensive conversion of the H_2O by the water–gas shift reaction would be required to stabilize Fe_3O_4 according to the CO_2/CO ratio. Typical CO conversions were generally much less than 20% in the present study. Hence, the H_2O/H_2 ratio appears to be the controlling factor since the sample was ca. 90% Fe_3O_4 after reaction at 508 K and ca. 100% Fe_3O_4 after reaction at 540 K in the H_2/CO gas mixture containing 2.7% H_2O. This agrees with the work of Schultz *et al.* (*37*).

It must now be explained why the sample treated at 543 K in H_2/CO was ca. 100% iron carbide. In view of the result that magnetite was stabilized by 2.7% H_2O in H_2/CO at this same reaction temperature, one possibility is that the water concentration dropped below this value during the 48 h treatment at 543 K. (Thermodynamically, the H_2O/H_2 ratio must be greater than ca. 0.019 for magnetite to be the stable phase of iron at 543 K (*8*).) A possible explanation for this behavior is that the sites active for the Fischer–Tropsch reaction became blocked by carbon deposited on the surface at 543 K. This is widely accepted as a means of deactivation for Fischer–Tropsch synthesis catalysts (*2*, *23*, *38*). As the active sites became blocked by carbon, the amount of H_2O produced dropped below the concentration required to stabilize Fe_3O_4, and iron carbide was formed. Another possibility is that at 540 K, the rates of CO dissociation and iron carbidization are much faster than the rate of H_2O formation via Fischer–Tropsch synthesis. Thus before sufficient water is formed to stabilize Fe_3O_4, Fe is carbided and then Fe_3O_4 formation is precluded. However, if H_2O is already present in the feed, then Fe_3O_4 is stabilized and carbide formation is slowed and probably limited.

The results of N_2O surface oxidation studies on the toluene-washed, unpromoted samples indicate that compared to Fe_3O_4, N_2O reactivity is lower with the sample treated in H_2/CO at 543 K and higher with the sample treated at 508 K. The Mössbauer spectrum of the latter sample was composed of primarily Fe_3O_4 with about 10% iron carbide; however, N_2O reactivity was greater than that for either pure Fe_3O_4 or samples composed of 100% χ-Fe_5C_2. The high reactivities with N_2O observed for the samples treated at 508 K are suggested to be due to the oxidation of "reduced iron species" which were active for Fischer–Tropsch synthesis. The low extents of N_2 formation for the samples treated at 543 K, and consisting of 100% iron carbide, are attributed to the slow oxidation of Fischer–Tropsch sites which were blocked by carbon. Washing these latter samples with toluene did not restore the reactivity of these sites for reaction with N_2O (i.e., these sites were blocked by carbon which could not be removed by the toluene wash). In contrast, the toluene wash increases the reactivity toward N_2O of the sample treated at 508 K. Apparently, removable wax on the reduced iron species of this sample decreases the reactivity of these sites for reaction with N_2O at room temperature.

The above arguments are in agreement with others (e.g., *23*) who have speculated that the active sites for Fischer–Tropsch synthesis are iron atoms on the surface. Iron atoms would be oxidized by N_2O to a greater extent than Fe_3O_4. Furthermore, according to the "competitive model" put forth by Niemantsverdriet *et al.* (*5*), the active iron sites are converted to iron carbide and subsequently blocked by inactive carbon during Fischer–Tropsch synthesis. In particular, as long as the catalyst has not been completely converted to iron carbide, carbon may diffuse into the bulk thereby minimizing the accumulation of "inactive" carbon on the surface. After the bulk has been saturated with carbon, the accumulation of this inactive carbon leads to catalyst deactivation. In the present study, high reactivities with respect to N_2O were observed for all samples composed of both magnetite and iron carbide. Accordingly, the reduced iron species on the surfaces of these samples were not blocked by inactive carbon since the bulk crystallites of these samples were not saturated with carbon. The low reactivity with N_2O of the samples composed of 100% iron carbide can be similarly interpreted in terms of the accumulation of inactive carbon on the surface since these samples were saturated with carbon. Finally, it should be noted that the results of this study are in agreement with the observations in the literature that the activity and selectivity for Fischer–Tropsch synthesis over iron are similar over catalysts containing different relative amounts of magnetite and iron carbide (*7*). In short, reduced iron species free of inactive carbon deposits are present on all of these catalysts containing magnetite and iron carbide. Finally, we note that by "reduced iron species" we do not necessarily suggest that these are metallic iron sites. The sites are more reduced than those on the surface of magnetite and may be intermediate surface carbides or oxides (*7*).

Potassium-Promoted Iron Samples

It has been shown that by measuring the extent of surface oxidation by N_2O, the surfaces of samples which were treated at different temperatures could be differentiated. The N_2O surface reaction studies are also sensitive to effects of the potassium promoter.

Qualitatively, the extents of surface oxidation by N_2O showed similar trends for both the promoted and unpromoted samples. Samples treated at temperatures above 540 K showed low N_2O reactivity whereas samples treated below 515 K had high N_2O reactivity.

As seen in Fig. 5, for samples treated at temperatures below 515 K, the potassium promoter had little effect on the extent of surface oxidation by N_2O. This is probably because the reduced iron species on the samples are fully oxidized by N_2O, with or without the presence of the promoter. However, addition of the potassium promoter apparently increased the reactivity of the sample toward N_2O after treatment at 543 K in H_2/CO. In fact, the amount by which the extent of N_2 formation increased upon potassium promotion was equal to the number of potassium cations added. Since it was shown that potassium cations do not react with N_2O at room temperature, potassium species either apparently increase the reactivity of surface sites or prevent extensive carbon contamination of these sites. In a similar fashion, King and Peri (*39*) observed that potassium increased the extent of nitric oxide (NO) dissociation on iron.

In agreement with the work of Pichler and Merkel (*26*), addition of the potassium promoter was observed to increase the rate of iron carbide formation. After 48 h of reaction at 508 K, the unpromoted sample was about 10% iron carbide. The promoted sample was about 50% iron carbide after 48 h of CO/H_2 treatment, even though the reaction temperature was 15 K lower. This may be an indirect consequence of the effect of the potassium promoter on the dissociation of adsorbed CO on iron (*18, 20*). With more carbon present on the surface, the rate of bulk carburization may be enhanced. A second contributing factor which would increase the rate of bulk carburization would be the presence of smaller iron particles in the promoted sample. Raupp *et al.* (*35*), using Mössbauer spectroscopy, observed that small iron particles carbided faster than larger particles.

The Mössbauer spectra of the samples treated at temperatures above 540 K in Runs FeK-2, FeK-3, and FeK-4 are essentially indistinguishable. Also, these samples showed the same extent of surface oxidation by N_2O when compared on a per gram of precursor basis. In addition, it can be seen in Table 3 that the BET surface areas increased with time of treatment in H_2/CO. A semilog plot of the BET surface area versus the length of time that the sample was treated above 540 K gives a straight line. Such a correlation has been shown to be useful for predicting carbon deposition rates for catalysts treated under similar conditions (*40*). Moreover, the BET surface area for FeK-1, the sample which was not treated at elevated temperatures, intersected this line at very short times. Hence, this correlation implies that this sample, FeK-1, had a very small amount of carbon deposited on it. This sample showed only 4% Fe_3O_4 in its Mössbauer spectrum and yet it had a high reactivity toward N_2O. These results agree with the aforementioned model of Niemantsverdriet *et al.* (*5*), according to which "inactive" carbon will not be deposited on the surface until the sample has been completely carbided.

CONCLUSION

Nitrous oxide has been shown to be an effective surface probe of iron-based samples treated under Fischer–Tropsch synthesis conditions. The extent of surface oxidation by this molecule is low over iron carbide (presumably due to surface coverage by carbon), intermediate over magnetite, and high over samples which contain both magnetite and iron carbide. These latter samples apparently contain reduced iron species and little carbon on their surfaces.

Addition of potassium promoter (added as potassium carbonate) apparently increases the rate of iron carbide formation. Yet even after high temperature (540 K) CO/H_2 treatment and 100% carbide formation, surface reactivity toward N_2O is higher than when the promoter is not present. This suggests that the potassium promoter enhances the reactivity/availability of potential catalytic sites.

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