JOURNAL OF SOLID STATE CHEMISTRY **58**, 211–220 (1985)

Methanation Studies: Characterization of Some Iron Catalysts by X-Ray Diffraction and Curie Point Determinations

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Received October 1, 1984; in revised form December 3, 1984

Methanation studies have been carried out at 290°C in a microreactor with a H_2/CO ratio of 9/1. The catalysts studied were iron(III) oxide, iron(II) diiron(III) tetroxide, and metallic iron. These were all prepared reproducibly from iron(III) nitrate. The catalysts were characterized by X-ray diffraction and magnetic analysis both at maximum activity and after deactivation. All catalysts at maximum activity contained Fe_5C_2. Deactivation of the catalysts was found to be due to excess graphitic carbon. Sustained catalytic activity was found to require the presence of iron(II) diiron(III) tetroxide, probably to serve as a source for continual renewal of the active catalyst surface. © 1985 Academic Press, Inc.

Introduction

The behavior of iron catalysts during the reduction of carbon monoxide by hydrogen has been investigated by numerous laboratories (*1–8*). It was shown (*7, 8*) that iron(III) oxide prereduced with hydrogen at 250°C reaches a maximum activity almost immediately when tested in a differential dynamic microreactor; however, the catalyst becomes deactivated in a relatively short period of time. Many investigators have attributed the loss of activity to the deposition of graphitic carbon on the surface of the catalyst.

There appears to be some controversy concerning the nature of the active catalyst. Raupp and Delgass (*2*), Amelse *et al.* (*1*), and Niemantsverdriet (*3, 4*) have claimed that iron carbide is a better catalyst than metallic iron. The increase in catalytic activity was related to the extent of carbide formation, and carbon incorporation into bulk iron particles controlled the concentration of the active surface sites. These research groups indicated that a positive correlation existed between the extent of carbide formation and the activity of the catalyst. However, Teichner and co-workers (*7, 8*) suggested that iron carbide is rapidly deactivated under synthesis conditions and that the active catalyst consists of iron in an oxide form. Their studies also indicated that the formation of graphitic carbon is decreased when the iron is in an oxidized state.

In spite of extensive literature dealing with iron catalysts, it is still not certain as

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0022-4596/85 $3.00

to the exact nature of the working catalyst. There have been relatively few studies in which the catalyst was related to the composition of the phases present. There are a number of problems associated with attempts to identify the active catalyst. Among these is the dependency of the activity on small changes in preparation of the working catalyst. Furthermore, a variety of phases have been associated with iron catalysts, including a mixture of iron oxides, iron carbides, α-iron and graphitic carbon. The relative ratio of these phases varies from one catalyst to another depending upon catalyst pretreatment, temperature and pressure of the reaction, conversion levels, and the hydrogen to carbon monoxide ratio.

Methanation studies, carried out by the reduction of carbon monoxide by hydrogen at ambient pressure, are useful in correlating catalyst activity with the nature of the active catalyst. Such studies yield molecules which are mainly small alkanes and alkenes (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8). The rather small number of products allows for ease of analysis and a good mass balance can be readily attained. The methanation reactions reported in this paper have utilized reproducible procedures for the preparation of Fe_2O_3, Fe_3O_4, and Fe. Reaction activity was related to the phase composition which was determined both by X-ray analysis and Curie point determinations of the magnetic phases present. It was expected that such correlations might provide further insight into the nature of the active catalyst.

Experimental

Iron(III) oxide (α-Fe_2O_3) was prepared by the decomposition of iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Fisher Certified). This was carried out in air by two successive heatings: 12 hr at 150°C followed by 24 hr at 400°C with intermittent grinding.

Iron(II) diiron(III) tetroxide (Fe_3O_4) was prepared in a glass reactor by the reduction of Fe_2O_3 at 400°C in an atmosphere of 98.8%/1.2% Ar/H_2 for 1.8 hr; the product was quenched under argon by removing the reactor from the furnace. This procedure has been described previously (*9*). X-Ray diffraction analysis indicated the presence of a single phase product.

Iron metal was obtained by the reduction of iron(III) oxide at 400°C for 24 hr under flowing hydrogen gas. The resulting product was allowed to cool to room temperature in the furnace under a hydrogen atmosphere. Thermogravimetric analysis of the iron oxides was performed by reduction with hydrogen at 800°C employing a Cahn electrobalance (Model 2000).

The catalysts were prepared for evaluation by cold pressing 200-mg portions at a pressure of 90,000 psi for the oxides and 30,000 psi for the metal. The resulting pellets were sieved to a size of 20–60 mesh. Surface area was measured by the BET method using a Quantasorb Surface Area Analyzer (Quantachrome Corporation). Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high intensity Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). For qualitative identification of the phases present, the patterns were taken from $30° < 2\theta < 50°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr. Scherrer's equation was used to determine the crystallite size. The integral half-widths of the diffraction peaks were obtained from X-ray patterns taken from $20° < 2\theta < 70°$ with a scan rate of 0.25° 2θ/min and a chart speed of 30 in./hr.

Curie point determinations of Fe_5C_2 and Fe_3C were made using a Faraday balance (*10*) equipped with a high-temperature heater. Samples were sealed in evacuated glass bubbles in order to prevent any decomposition upon heating. The sealed sample was heated in an atmosphere of 40 Torr helium from room temperature to 500°C at a

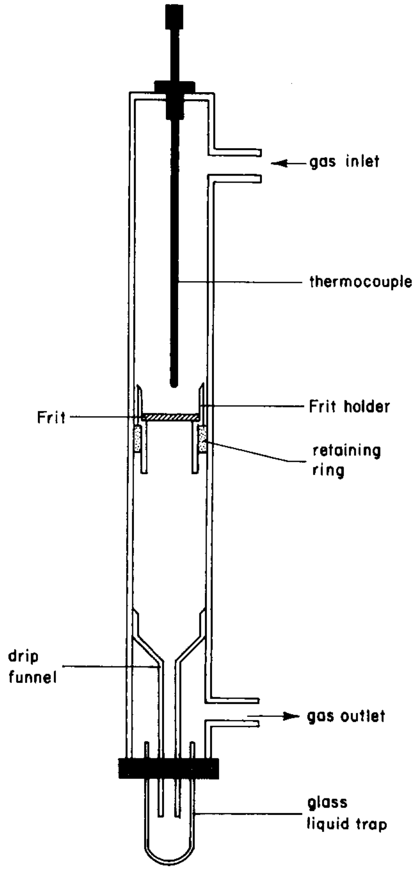

FIG. 1. Fischer–Tropsch microreactor used for methanation.

rate of 30°C/min. The relative magnetization (at a constant field strength of 100 Oe) was recorded as a function of temperature using a Bascom–Turner Acquisition Center, Model 4110.

The reactor system consisted of a gas feed section, a reactor (shown in detail in Fig. 1), and a gas chromatograph. The complete system, including all tubing, fittings and valves, was made of stainless steel. The reactor was a fixed-bed microreactor made of ½-in. o.d. stainless steel tubing. The catalyst was supported on a ⅜-in. 40-μm stainless-steel porous frit contained in a holder which pressed into the reactor tube so that the gas flowed through the catalyst bed. The reactor was heated by a furnace and the temperature was controlled by a Research Incorporated Type MPRY controller. The temperature of the catalyst bed was monitored by an Omega 316 S.S. sheathed Type K thermocouple positioned directly above the catalyst bed. All experiments were carried out at ambient pressure, a reactor temperature of 290°C, and a H_2/CO ratio of 9/1. The total flow rate of the feed gas was 60 cm^3/min. The gases hydrogen (Matheson, ultrahigh purity), an 81%/19% carbon monoxide/helium mixture (Matheson >99.99%), and argon (Matheson, ultrahigh purity) were used as supplied. The helium in the carbon monoxide was used as an internal standard to monitor any pressure drop resulting from the chemical reaction of the synthesis gas over the catalyst.

In a typical experiment 0.5 g of catalyst (20–60 mesh) was loaded into the reactor. For most reactions studied, the system was initially purged with argon at room temperature and the catalyst was then heated to 290°C over a 45-min period under a flow of argon (60 cm^3/min). Methanation studies were then carried out with the rates of flow of both H_2 and CO/He gases regulated by mass flow controllers (Brooks 5850).

The exit gases were analyzed by means of a Varian Vista 6000 gas chromatograph fitted with a Poropak Q (80–100 mesh) 6 ft × ⅛ in. stainless-steel column and a Molecular Sieve 5A (45–60 mesh) 6 ft × ⅛ in. stainless-steel column. Liquids produced in the reaction were condensed out in a cold trap and analyzed by a second Poropak Q (80–100 mesh) 6 ft × ⅛ in. stainless-steel column. For the reaction conditions used, only water was found. A mass balance computer program was used to calculate the mass balance of the reactants and products obtained from each sampling.

Results and Discussion

Iron(III) oxide samples were prepared by

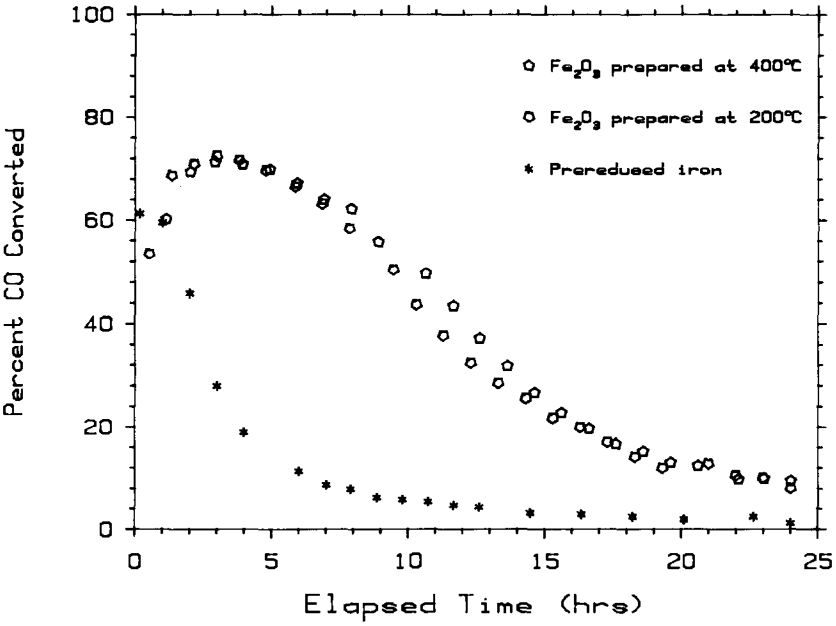

FIG. 2. Catalytic activity (percentage of CO converted) as a function of time for 500-mg samples of Fe_2O_3 catalyst prepared at 400 and 200°C and of prereduced iron catalyst. The conditions of methanation were: ambient pressure, reactor temperature of 290°C, H_2 to CO ratio of 9/1, and gas flow of 60 cm^3/min.

preheating $Fe(NO_3)_3 \cdot 9H_2O$ at 150°C followed by a final heating at temperatures between 200 and 600°C. The crystallite sizes of the resulting iron oxide particles varied between 100 and 440 Å. The samples chosen for the methanation studies were prepared at 200°C (100 Å) and 400°C (200 Å). Methanation studies were carried out at 290°C and the percent of CO conversion as a function of time is given in Fig. 2 for these iron(III) oxide samples. At temperatures lower than 290°C, methane production was low and the reactions proceeded slowly. Reymond *et al.* (*8*) have shown that at 250°C, with a H_2/CO ratio of 9/1, at 1 atm pressure and a flow rate of 60 cm^3 min^{-1}, the total conversion of CO was less than 5%. However, the weight of catalyst was 50 mg which is one-tenth of the quantity used in this study. When carbon monoxide was reduced at 250°C, but under all other reactor conditions described in this study, the total maximum conversion of CO was 20%, compared to 70% achieved at 290°C. At higher temperatures than 290°C, the reaction rates were too fast and deactivation of the catalyst occurred very rapidly. At H_2/CO ratios less than 9/1, conversions were low and deactivation also took place too rapidly. At higher H_2/CO ratios, deactivation proceeded too slowly to be adequately characterized within a 24-hr period.

It can be seen from Fig. 2 that the percent of CO conversion reaches a value of over 70% in 4 hr and decays to only 10% in 24 hr. The methane production shows a behavior similar to that observed for CO consumption. Whereas the absolute value of CH_4 produced decreases rapidly with time, it can be seen from Fig. 3 that the percentage of methane in the converted CO does increase. Figure 3 also shows that the concentrations of the olefins C_2H_4 and C_3H_6 also increase with time. These changes may

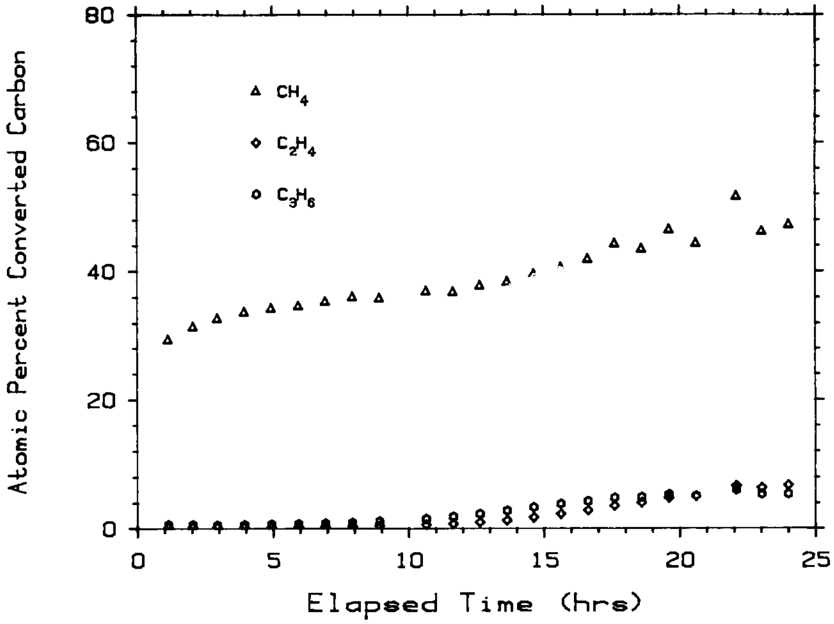

FIG. 3. Product concentrations expressed as atomic percentage of the converted carbon for CH_4 and the olefins C_2H_4 and C_3H_6 as functions of time for Fe_2O_3 catalyst.

be related to secondary hydrogenation reactions at high conversions, as well as to changes in the catalyst as deactivation proceeds. The value of α which is obtained from Schulz–Flory plots (Fig. 4) decreases from a value of 0.33 at maximum activity to 0.25 for the spent catalyst. Such low values of α are expected (*11*) because small chain lengths are produced when the reduction of CO is carried out at ambient pressure with bulk unpromoted iron oxide.

It was anticipated that the crystallite size of the working catalyst should be related to the size of the Fe_2O_3 crystallites. Hence, Fe_2O_3 prepared with the final decomposition temperature of the nitrate at 200°C (100 Å) should result in smaller catalyst particles than from Fe_2O_3 prepared at a final temperature of 400°C (200 Å). As is shown in Table I, the differences in crystallite sizes of the actual phases present in the reactor at maximum activity are far less than expected. There is, in fact, little difference in either the crystallite sizes or the surface areas of the Fe_3O_4, Fe_5C_2 catalysts prepared from iron oxide particles with large differences in crystallite size. There should, therefore, be little difference in the measured catalytic activity and this is what was observed (Fig. 2).

The working catalyst was examined by X-ray diffraction analysis and Curie point determinations were made with a Faraday balance. These results are given in Figs. 5 and 6. It can be seen that the composition of the catalyst at maximum activity (3–4 hr)

TABLE I

CATALYST AT MAXIMUM ACTIVITY (COMPOSITION: Fe_3O_4, Fe_5C_2)

Temperature (°C) of preparation of Fe_2O_3 (starting material)	Crystallite size by X ray (Å)		Surface area by BET (m^2/g)
	Fe_3O_4	Fe_5C_2	
200	215	150	14.6
400	230	190	12.5

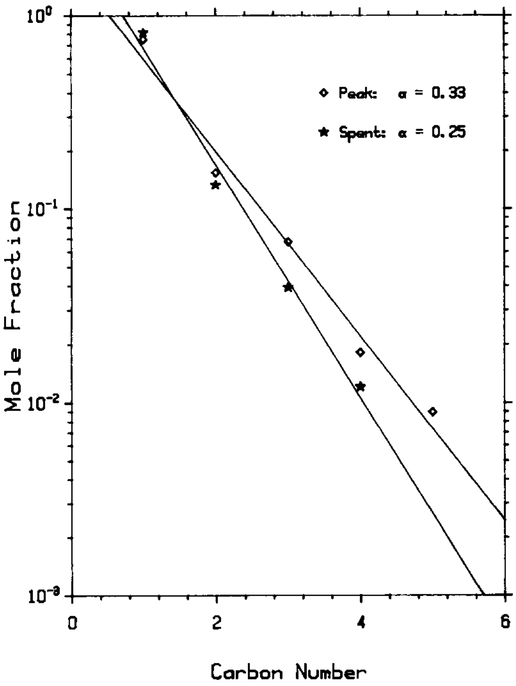

FIG. 4. Schulz–Flory plot of the methanation product concentrations as functions of carbon number for 500 mg of Fe_2O_3 catalyst at maximum activity and after deactivation.

consisted of approximately 75% Fe_3O_4 and 25% Fe_5C_2, whereas the spent catalyst (after 4 hr) showed only the presence of Fe_5C_2. Total carbon could be determined by heating the spent catalyst in a stream of pure hydrogen at 800°C. This procedure stripped the carbon and gave a product which analyzed as α-Fe. Results of such analyses indicated that the spent catalyst contained 10 wt% of free carbon in excess of the carbon associated with the Fe_5C_2 phase. Although it was not possible to analyze the percent of free carbon associated with the catalyst at maximum activity because of the presence of oxide, it does appear that a considerable quantity of carbon is present in the spent catalyst. These results are in agreement with those of Bonzel and Krebs (*12*, *13*), who have shown that metallic iron is catalytically active but is rapidly deactivated by carbon deposition.

Magnetite, Fe_3O_4, is formed almost immediately when Fe_2O_3 is placed in the methanation reactor. Hence Fe_3O_4 should give the same results as to activity and phase composition. The results obtained in this study were substantially the same as those obtained for Fe_2O_3, which is consistent with the observation that Fe_2O_3 is immediately reduced to Fe_3O_4 under methanation conditions.

Pure iron was prepared by the reduction of Fe_2O_3 in a hydrogen atmosphere at 400°C for 24 hr. The product was transferred to the reactor, heated in a hydrogen atmosphere to 290°C at 6°C/min, and then the methanation process was started. It can be seen from Fig. 2 that the maximum activity for CO conversion was reached at the first sampling, which took place 10 min into the

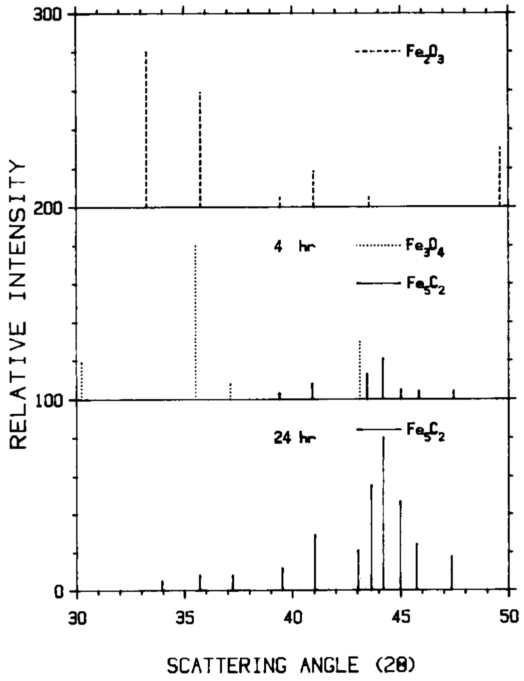

FIG. 5. X-Ray diffraction patterns for Fe_2O_3 catalyst when fresh, at maximum activity (4 hr), and after deactivation (24 hr).

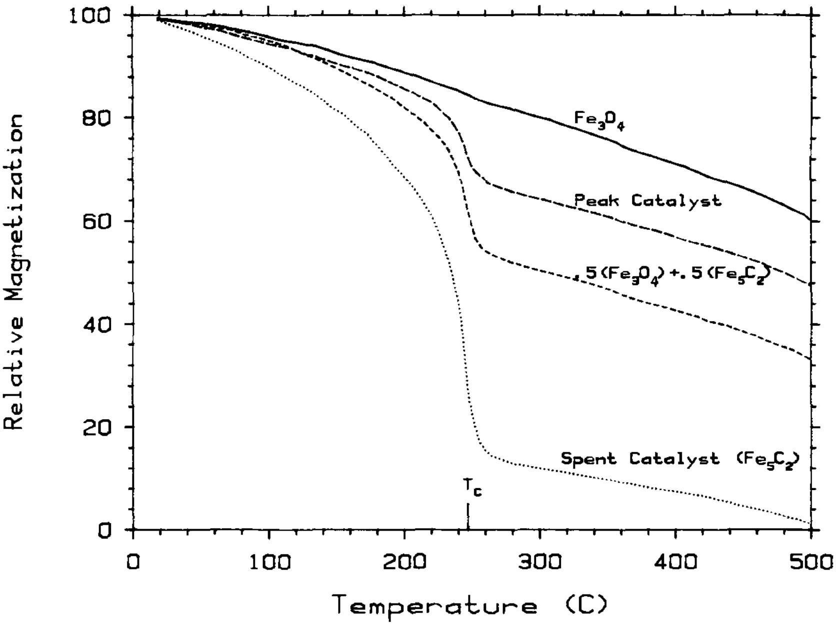

FIG. 6. Variation of magnetization with temperature in a field of 100 Oe for Fe_2O_3 catalyst at maximum activity and after deactivation. Corresponding data for pure Fe_3O_4 and for 50/50 mixture of Fe_3O_4/Fe_5C_2 is shown for quantitative comparison.

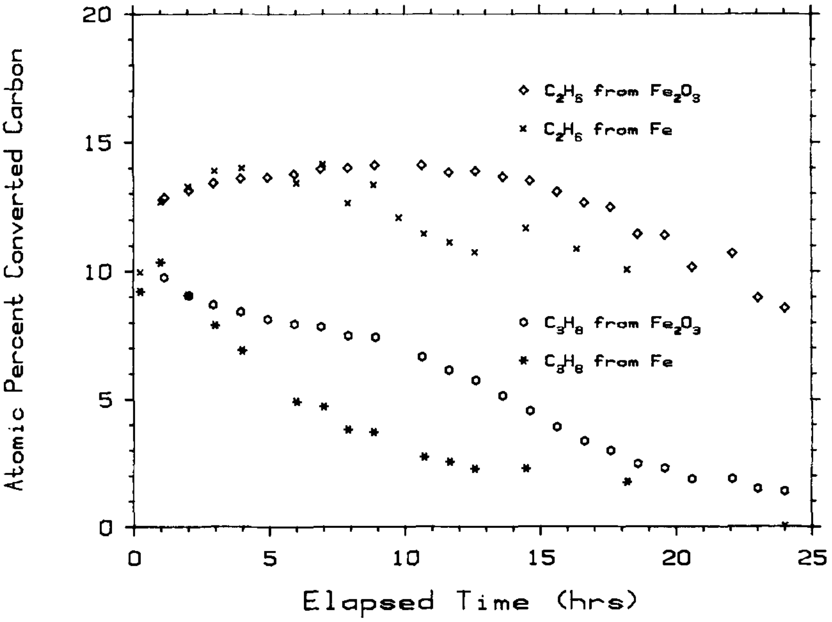

FIG. 7. Variation with time of the product concentrations (expressed as atomic percentage of the converted carbon) of saturated hydrocarbons for 500 mg of Fe_2O_3 and of prereduced iron catalysts under the conditions of methanation.

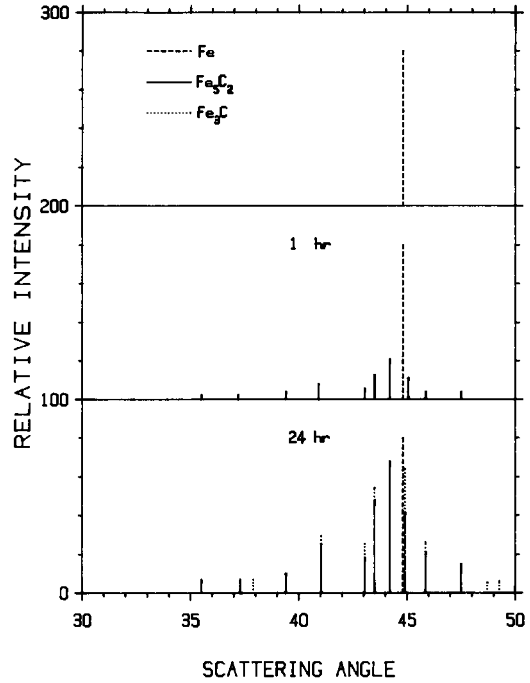

FIG. 8. X-Ray diffraction patterns for prereduced iron catalyst when fresh, near maximum activity (1 hr), and after deactivation (24 hr).

run; the conversion then declined rapidly. This also occurred for methane production. The methane and olefin product percentage increased with time in a manner similar to the increase shown in Fig. 3 for iron(III) oxide. However, as seen in Fig. 7, the saturated hydrocarbons C_2H_6 and C_3H_8 decreased more markedly with time than occurred when iron oxide catalysts were used. Hence it appears that iron oxides are necessary components for sustaining catalytic activity. When prereduced iron was used as the catalyst, the α value obtained at maximum activity was 0.39 and this decreased to a value of 0.17 for the spent catalyst. This lower value for α after 20 hr of CO reduction is consistent with the higher methane and more marked decrease in the C_2H_6 and C_3H_8 production.

The phases Fe_5C_2 and Fe were detectable both on X-ray diffraction patterns and from thermomagnetic curves taken from products which were quenched after 10 min of reaction time (at maximum activity). After 24 hr a considerable quantity of Fe_3C was observed to be present in the X-ray diffraction spectra (Fig. 8). Magnetic measurements of the spent catalyst clearly show in Fig. 9 the two Curie points for Fe_5C_2 and Fe_3C. It has thus been shown that the active catalysts formed from both Fe_2O_3 and metallic iron contain Fe_5C_2. Catalyst deactivation is most probably associated with the unreactive graphitic carbon which is formed during the methanation process. A more sustained activity was observed when iron oxide was still present in the working catalyst. It is evident that fresh catalyst is being continually produced as long as a source of reducible iron oxide is present and the absence of oxide results in rapid catalytic deactivation.

Methane appears to form via a surface carbide mechanism first proposed by Fischer and Tropsch (*14*) in 1926. This mechanism has been reviewed by Biloen and Sachtler (*15*) as well as Dwyer and Hardenbergh (*16*). In this mechanism, iron carbide is formed as a result of diffusion of carbon into the bulk iron particles. In this study when Fe_2O_3 is used as the starting material, at maximum activity approximately 25% of the catalyst was identified as Fe_5C_2. Even for pure iron as the starting catalyst, Fe_5C_2 was observed to form immediately under reaction conditions. However, it is still not clear whether the active catalyst is metallic iron and/or iron carbide Fe_5C_2. The carbon atoms which are formed from CO can also react with each other to form unreactive graphitic carbon. From reduction studies of the spent catalyst, it was observed that excess graphitic carbon was present which is consistent with the model proposed by Fischer and Tropsch.

The molecules produced over the iron powders are mainly methane and other small alkanes. Although some chain build-

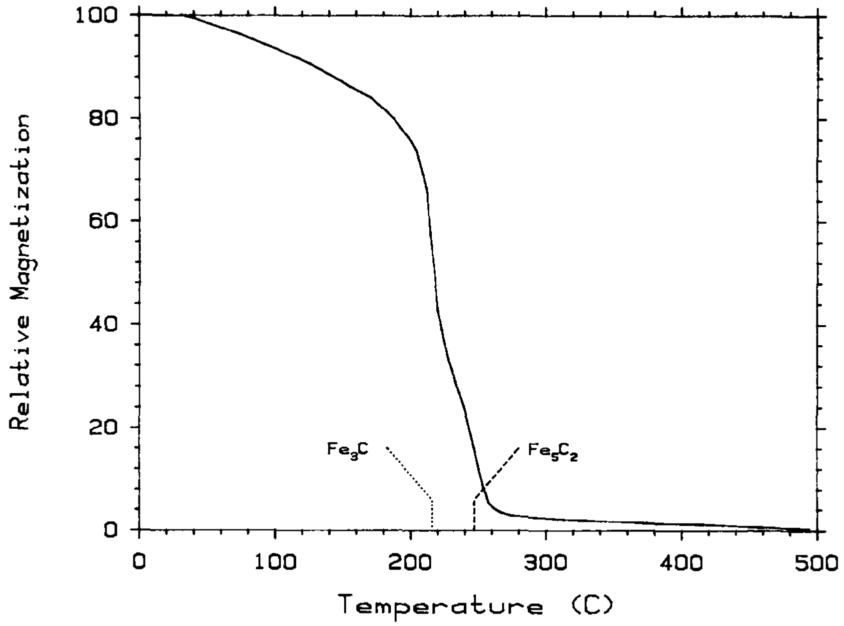

FIG. 9. Variation of magnetization with temperature in a field of 100 Oe for prereduced iron catalyst after deactivation. The presence of two phases having Curie temperatures which correspond to Fe_3C and Fe_5C_2 is indicated.

ing occurs ($\alpha = 0.39$ at maximum activity) the product distribution in these studies is not typical of true Fischer–Tropsch chemistry ($\alpha > 0.65$) where the majority of products are liquid and solid hydrocarbons.

It should be noted that these studies were carried out on bulk iron catalysts but nevertheless are consistent with the carbide model.

Summary and Conclusions

Methanation studies were carried out starting with iron(III) oxide, iron(II) diiron (III) tetroxide, or metallic iron as the initial catalysts. Under the conditions used in this study, there was little difference in the crystallite size, surface area or activity of the working catalysts (Fe_3O_4, Fe_5C_2) prepared from iron oxide particles with large differences in crystallite size. Characterization of the catalysts at maximum activity and when deactivated was achieved by X-ray diffraction analysis and thermal magnetization studies. In addition, the deactivated catalyst contained a large excess of unreactive graphitic carbon.

Magnetite gave the same results as Fe_2O_3 with respect to both catalytic activity and phase composition. This is consistent with the observation that magnetite (Fe_3O_4) is formed as an intermediate when Fe_2O_3 is placed in the methanation reactor. Prereduced Fe deactivates much more rapidly than either of the oxides. It appears that magnetite is necessary for sustained catalytic activity—probably because it is a source for continual renewal of the working catalyst surface. However, the results reported in this paper do not establish whether this active catalyst is active surface iron or Fe_5C_2.

It should be noted that these observations are based on bulk sample studies carried out at 290°C where the rate of conversion of CO is relatively high. The phenomenon will be altered at other temperatures. However, it is important to distinguish between those phenomena which occur in bulk samples and those which may be influenced by unique surface chemistry.

Acknowledgments

Acknowledgment is made to the Office of Naval Research for support of K. Dwight and partial support of L. Carreiro, and to the National Science Foundation (DMR-82-03667) for the support of Y.-T. Qian and J. Fournier. Partial support of this research was also provided by Exxon Education Foundation and the authors wish to thank Dr. Rocco Fiato of Exxon Research Laboratories, Clinton, New Jersey, for his help in the design of the equipment. In addition, appreciation is expressed for the use of Brown University's Materials Research Laboratory which is supported by the National Science Foundation.

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