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# The Role of pH in the Performance of Precipitated Iron Fischer–Tropsch Catalysts[1]

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Precipitated iron Fischer–Tropsch catalysts were prepared at various constant pH levels with a Kölbel in-line mixing unit using either sodium carbonate or ammonium hydroxide as the precipitant. In microreactor studies at 1.38 MPa and 548 K, the $Na_2CO_3$-precipitated catalysts prepared at low pH (3.7 and 4.7) showed unusually high olefin selectivity ($C_2$–$C_4$) as well as activity maintenance superior to that of the catalysts prepared at higher pH (5.8, 7.6, and 9.8). While the $NH_4OH$-precipitated catalyst showed lower olefin selectivity, the activities of these catalysts, especially the copper-promoted ones, were quite stable for periods of up to 300 h. Thermogravimetric studies indicated that graphitic carbon deposition occurred to a greater degree on $Na_2CO_3$-precipitated catalysts prepared at high pH. The high soda content of these catalysts was identified as one factor accounting for this deposition and presumably also accounted for the higher rates of deactivation. Those factors responsible for the high olefin selectivity of the $Na_2CO_3$-precipitated catalysts prepared at low pH remain unidentified.

## INTRODUCTION

One approach of current interest in indirect liquefaction is the charging of the total Fischer–Tropsch (F-T) reactor effluent (uncooled) into a second reactor containing a shape-selective zeolite (*1*). The goal of indirect liquefaction is to maximize the production of liquid transportation fuels; therefore, it is desirable to minimize the methane yield and maximize the $C_2$–$C_4$ olefin yield in the F-T product. The light olefins can be upgraded readily to gasoline over the zeolite catalyst. The objective of this paper was to investigate certain variables involved in the preparation of precipitated iron F-T catalysts to determine if improvements could be made in the product selectivity of the F-T product so as to maximize eventual liquid hydrocarbon yield. Numerous studies have been carried out with these catalysts since the discovery of F-T synthesis in 1923; however, except for the extensive studies reported by the Bureau of Mines in the period 1940–1965 (*2*), few papers describe the effect of the precipitation step itself on the performance of these catalysts. In particular, the role of the pH in the precipitation step has been considered by only a few investigators. Parkash (*3*) investigated the changes in pore structure of precipitated iron catalysts during pretreatment and synthesis reactions involving CO and steam. Rähse and co-workers (*4*) found an optimum pH for CO conversion, but no mention was made of selectivity. In addition, since these catalysts were prepared by adding sodium carbonate solution to an iron nitrate solution, the pH was not constant during the precipitation step. Dry (*5*) found that the pore volume and pore size distribution were largely determined in the very first stage of the catalyst preparation, i.e., the precipitation of the iron. The pore size distribution was influenced by (1) the concentrations of the solutions used, (2) the time over which the precipitation occurred,

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[1] Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply endorsement or favoring by the United States Department of Energy.

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(3) the precipitation temperature, and (4) the pH during precipitation. In addition, a significant difference in pore size distribution resulted if the manner of solution addition was reversed, i.e., iron nitrate solution was added to a solution of sodium carbonate. Again the pH varied during the precipitation step regardless of the manner of solution addition. Thus, one problem with the previous studies is that the pH was not held constant but changed throughout the precipitation step. The effect of pH on the physical structure and ultimate catalyst activity and selectivity thus remains uncertain.

We report here the preparation and characterization of a series of precipitated iron catalysts, along with measurements of their activity and selectivity in Fischer–Tropsch synthesis. Like the previous studies, the pH of precipitation was the main parameter varied during preparation of these catalysts. However, unlike the previous studies, the pH was held constant during precipitation, so the effect of pH on catalyst structure and F-T synthesis behavior could be determined.

## EXPERIMENTAL

The catalysts were prepared using a continuous in-line mixing unit similar to that described by Kölbel (*6*) and Deckwer (*7*). Into this unit a solution of $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water (7.4 wt%) was co-fed with a solution of either $Na_2CO_3 \cdot H_2O$ (4.6 wt%) or $NH_4OH$ (10 wt%) in distilled water. The copper-promoted catalysts were prepared by adding $Cu(NO_3)_2 \cdot 3H_2O$ (1.15 wt%) to the iron nitrate solution. Before mixing, the solutions were heated to 348–353 K ($NH_4OH$, to 333 K). Catalysts were prepared at different pH by varying the flow rates of the solutions. Since filtration of the gel proceeded slowly, no attempt was made to regulate the residence time of the slurry in the mixer. Following precipitation, the catalysts were washed with 6 liters of distilled water at 347 K and dried in air at 383 K for 24 h. The catalysts were ground, and the −200 + 325 mesh fractions were used in the microreactor and characterization studies. About 100 g of catalysts were prepared at each pH. Catalysts in the remainder of this paper will be designated by the pH at which precipitation occurred followed by either SC or AH, indicating that either sodium carbonate or ammonium hydroxide was used as the precipitant. For example, catalyst 3.7 SC indicates the catalyst was prepared at a pH of 3.7 using sodium carbonate.

Microreactor studies were carried out in a 1/2-in.-o.d. stainless-steel reactor with a 1/16-in. Chromel–Alumel thermocouple inserted into a 1/8-in.-o.d. thermocouple well that extended 1/4 in. into the catalyst bed. The bed was held in place by means of glass wool and a 1/4-in.-diameter spacer at each end of the reactor. Typically, 0.25 g of the catalyst (−200 + 325 mesh) was intimately mixed with 1.75 g of a glass powder (−50 + 100 mesh); the glass powder was added to maximize heat loss through the reactor wall and to decrease the pressure drop over the bed. The synthesis gas flowed downward through the vertical reactor. A trap maintained at 273 K collected the liquid product. The product gas flow rate was monitored by a wet test meter; gas samples were analyzed for hydrogen, carbon monoxide, carbon dioxide, and $C_1$–$C_4$ hydrocarbons using gas chromatography. The liquid condensate in the trap was separated into an aqueous fraction and oil fraction. The aqueous fraction was analyzed by mass spectroscopy for oxygenates and water. Infrared absorption was used to obtain a semiquantitative measure of the functional group composition of the oil fraction. Product collection and analysis were carried out every 24 h.

Catalysts were activated by raising the reactor temperature at a rate of 2 K/min in flowing nitrogen (60 ml/min). At 473 K, the gas was switched to a mixture of 50% $H_2$ and 50% CO (60 ml/min) at 101 kPa. The temperature was raised to 548 K at a rate of 2 K/min; the reactor was maintained at this

TABLE 1

Elemental Analysis of Catalyst Samples (after Drying at 473 K)

| Sample | Weight percentage | | | Cu/Fe[a] | Na/Fe |
|---|---|---|---|---|---|
| | Fe | Cu | Na | | |
| 3.7 SC | 64.3 | 0.2 | 0.2 | 0.003 | 0.003 |
| 4.7 SC | 63.1 | 0.9 | 0.2 | 0.014 | 0.003 |
| 5.8 SC | 64.9 | 1.8 | 0.2 | 0.028 | 0.003 |
| 7.6 SC | 62.6 | 1.7 | 2.7 | 0.027 | 0.043 |
| 9.8 SC | 64.3 | 1.8 | 1.3 | 0.028 | 0.020 |
| 6.2 AH | 64.0 | —[b] | — | 0.000 | — |
| 7.6 AH | 64.4 | 0.3 | — | 0.005 | — |
| 8.9 AH | 66.3 | —[b] | — | 0.000 | — |

[a] If complete precipitation of both copper and iron salts occurred, the Cu/Fe ratio would be 0.030.

[b] Samples 6.2 AH and 8.9 AH were made with copper-free solutions.

temperature for 2 h. The reactor pressure was then increased to 1.38 MPa over a period of about 20 min. All gas volumes were measured at 298°K and 101 kPa.

The thermogravimetric data were obtained with a Perkin–Elmer TG-2 using platinum pans. The sample size ranged from 4 to 8 mg. The flow rate of the reactant gas into the sidearm of the unit was 150 ml/min. The balance mechanism was purged with 20 ml/min helium. Before activation, the samples were maintained at 473 K for 10 min in helium or until a constant weight was attained. The TGA data were obtained at atmospheric pressure.

Surface areas were obtained from $N_2$ physical adsorption by means of the BET equation using a Micromeritics 2500 unit. Pore size distributions were determined using the Kelvin equation. To prepare samples for these measurements, the samples were carbided using a procedure identical to that used in the microreactor studies except the final activation temperature was 523 K. After carbiding (or reducing) the sample and cooling it to room temperature, a mixture of 2% $O_2$ and 98% $N_2$ was flowed through the sample tube to "passivate" the sample. Thermogravimetric studies indicated that less than a 5% increase in weight occurred as a result of this treatment. After the sample was placed in the Micromeritics unit, the sample was evacuated at 523 K for 2 h.

The Fe(110) peak width at about $2\theta = 44.7°$, obtained with copper radiation, was used to calculate the crystallite size of samples reduced in $H_2$ at 523 K and then "passivated." The peak widths at half maximum were corrected for instrumental broadening before using them in the following relationship:

$$\text{Crystallite size (nm)} = \frac{0.9 \times \lambda \times 5.73}{\text{width} \times \cos\theta}, \text{ where } \lambda = 1.542$$

## RESULTS

### *Chemical Analysis of Samples*

The results of the chemical analyses are shown in Table 1. The low Cu/Fe ratios obtained for samples 3.7 SC and 4.7 SC indicate that precipitation of the copper was incomplete in acidic media (pH <6). The Na/Fe ratio also increased with the pH of precipitation. This is consistent with the work of Rähse (*8*), who found a similar dependence of alkali adsorption on pH. Rähse found that positively charged species of iron are formed in acidic media, and negatively charged species in alkaline media, with an isoelectric point at a pH of 6.7. Thus, in the present study, the sodium cation would not be attracted to the positively charged iron oxide gel formed in acidic media, and the Na/Fe ratios would be correspondingly low.

### *Surface Area and Pore Size Distribution*

The $N_2$ BET measurements were made on samples air-dried at 383 K for 24 h and, as described in the Experimental Section, on "passivated" carbided catalysts. The large surface areas and small pore diameters of the air-dried samples are similar to those reported in a previous study (*9*). The decrease in surface area and pore volume (see Table 2) that occurred during pretreat-

TABLE 2

BET Surface Area and Pore Volume of Precipitated Iron Samples

| pH | Air-dried at 383 K for 24 h | | Carbided at 523 K for 2 h | |
|---|---|---|---|---|
| | S. A. ($m^2/g$) | P.V. (ml/g) | S. A. ($m^2/g$) | P.V. (ml/g) |
| 3.7 SC | 160 | 0.21 | 24 | 0.12 |
| 4.7 SC | 244 | 0.25 | 21 | 0.10 |
| 5.8 SC | 267 | 0.34 | 63 | 0.19 |
| 7.6 SC | 148 | 0.20 | 45 | 0.18 |
| 9.8 SC | 225 | 0.28 | 54 | 0.18 |
| 6.2 AH | 229 | 0.31 | 46 | 0.16 |
| 7.6 AH | 264 | 0.30 | 62 | 0.18 |
| 8.9 AH | 238 | 0.33 | 39 | 0.16 |

ment in synthesis gas was due only partly to sintering at 523 K because treatment of these samples in $N_2$ at 523 K resulted in little change in surface properties. The surface area and pore volume obtained following pretreatment of samples 5.8 SC and 7.6 SC in air and in hydrogen are shown in Table 3.

The pore size distributions for samples 3.7 SC and 9.8 SC, after carbiding, are shown in Fig. 1. While the plots for samples 4.7 SC, 5.8 SC, and 7.6 SC are not shown, there is little difference in pore size distributions for these five samples. The pore size distributions for sample 7.6 AH and 8.9 AH after carbiding are shown in Fig. 2. The

TABLE 3

BET Surface Area and Pore Volume after Pretreatment in Various Gases at 523 K for 2 h

| Gas | Surface area ($m^2/g$) | | Pore volume (ml/g) | |
|---|---|---|---|---|
| | 5.8 SC | 7.6 SC | 5.8 SC | 7.6 SC |
| Air (383 K) | 267 | 148 | 0.34 | 0.20 |
| $N_2$ | 234 | 143 | 0.34 | 0.19 |
| $H_2$ | 46 | 41 | 0.18 | 0.17 |
| 50% $H_2$–50% CO | 53 | 45 | 0.19 | 0.18 |

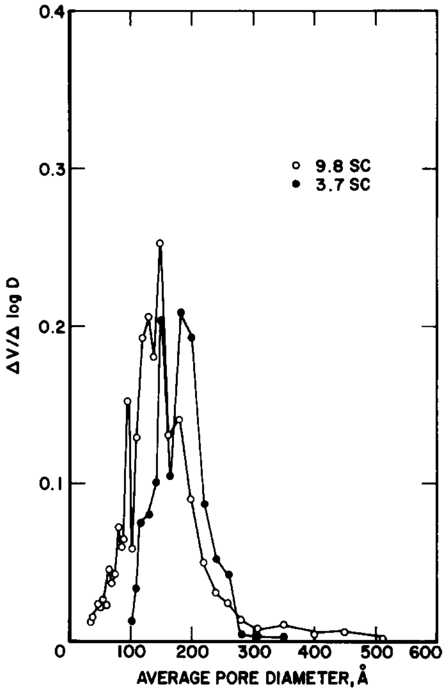

FIG. 1. Pore volume distribution for samples 3.7 SC and 9.8 SC after carbiding in 50% $H_2$–50% CO for 2 h at 523 K.

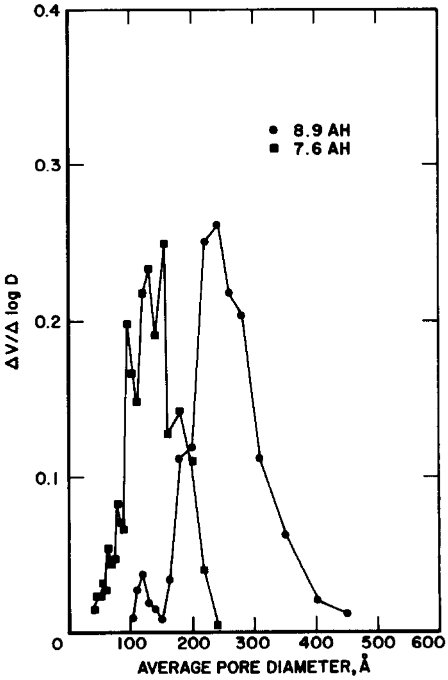

FIG. 2. Pore volume distribution for samples 8.9 AH and 7.6 AH after carbiding in 50% $H_2$–50% CO for 2 h at 523 K.

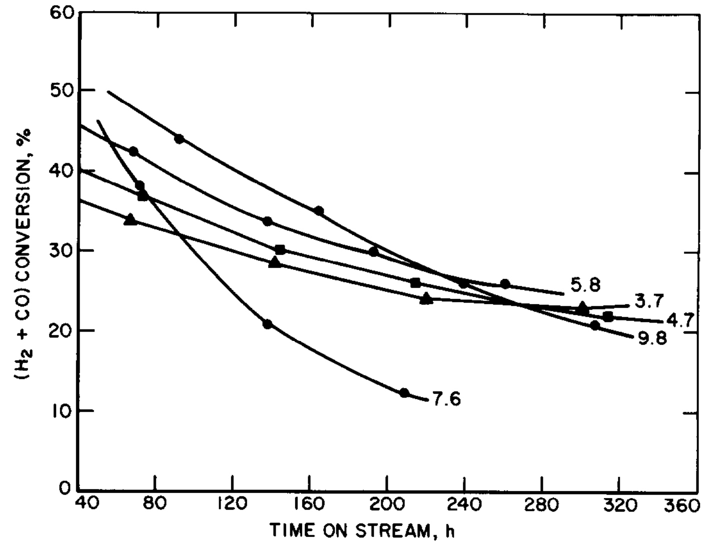

FIG. 3. Synthesis gas conversion for $Na_2CO_3$-precipitated catalysts.

pore size distribution for carbided 6.2 AH was intermediate between these two samples.

### X-Ray Diffraction

X-Ray diffraction studies were carried out on samples that had been heated to 473 K in air for 2 h. The only phase identified was $\alpha$-$Fe_2O_3$; the degree of crystallinity ranged from a high of about 30% for samples prepared at high pH (7.6 SC and 9.8 SC) to about 10% for samples prepared at the lower pH levels (3.7 SC and 4.7 SC). The error in these measurements was about 10% (abs.). It was not clear from these measurements if the low crystallinity was due to very small (<4 nm) crystallites of $\alpha$-$Fe_2O_3$ or to the presence of noncrystalline material.

The average crystallite size of samples reduced in $H_2$ for 2 h at 548 K ranged from 28.0 to 33.0 nm. No trend with pH was observed. While these samples were "passivated" after reduction, no peaks due to iron oxide were found in the diffraction patterns.

### Microreactor Testing

Each catalyst was tested for up to 300 h on stream at 548 K and 1.38 MPa and at a GHSV = 14.4 liters $h^{-1}$ $g^{-1}$. As the data in Fig. 3 indicate, partial deactivation of these catalysts occurred, especially during the first 100 h on stream. While the initial conversions were highest for catalysts 7.6 SC and 9.8 SC, these high pH catalysts deactivated most rapidly, with the result that after 200 h on stream, they were less active than the low pH catalysts 3.7 SC and 4.7 SC. There was a small change in hydrocarbon selectivity, with the product becoming heavier and less olefinic with increasing time on stream. These selectivity changes were typical of all five catalysts.

The light hydrocarbon selectivities for each catalyst after 200 h on stream are shown in Table 4. Of considerable significance is the more than twofold variation in the olefin/paraffin ratio for the $C_2$–$C_4$ fraction and the corresponding decrease in the yield of $C_1$–$C_4$ saturates.

Oxygenates in the aqueous fraction consisted primarily of ethyl alcohol and acetic acid, with smaller amounts of methanol, *n*-propanol, *n*-butanol, isopropyl alcohol, and acetone. These oxygenates in the aqueous layer accounted for 4 to 7% of the total hydrocarbons and oxygenates formed.

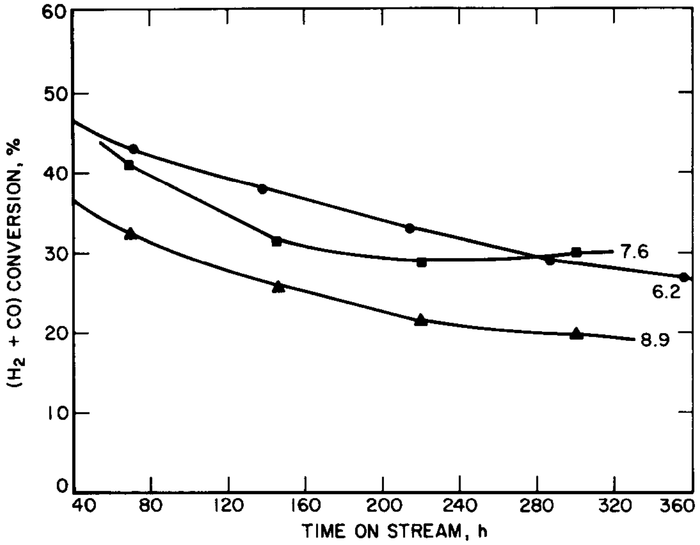

FIG. 4. Synthesis gas conversion for $NH_4OH$-precipitated catalysts.

### $NH_4OH$-Precipitated Catalysts

These catalysts deactivated less rapidly than the catalysts prepared using sodium carbonate. In particular, the copper-promoted catalyst 7.6 AH exhibited activity maintenance as good as that of any of the eight catalysts tested (see Fig. 4). The reaction conditions were the same as those described previously. There was little change in hydrocarbon selectivity according to carbon number with increasing time on stream; a small increase in the olefin/paraffin ratio of the $C_2$–$C_4$ fraction was found with time on stream. The olefin/paraffin ratios for each catalyst after about 200 h on stream are reported in Table 5.

TABLE 4

Light Hydrocarbon Selectivity as a Function of pH of Precipitation ($Na_2CO_3$)

| pH | Olefin/paraffin[a] ($C_1$–$C_4$ fraction) | $CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$ |
|---|---|---|
| 3.7 | 9.8 | 6.4 |
| 4.7 | 6.2 | 7.4 |
| 5.8 | 4.3 | 13.5 |
| 7.6 | 4.2 | 10.9 |
| 9.8 | 4.4 | 12.7 |

[a] Selectivities (wt%) were determined after 200 h on stream.

### Thermogravimetric Studies

In addition to the X-ray diffraction studies, thermogravimetric studies were carried out on the catalysts in various atmospheres and temperature ranges. In these TGA runs, the temperature was first increased to 548 K in He and then held at that temperature for 5–10 min until a constant weight was attained. Although microreactor studies were carried out by activating the samples in a mixture of 50% $H_2$ and 50% CO

TABLE 5

Light Hydrocarbon Selectivity[a] as a Function of pH of Precipitation

| pH | Olefin/paraffin[a] ($C_1$–$C_4$ fraction) | $CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$ |
|---|---|---|
| 6.2 AH | 4.6 | 10.2 |
| 7.6 AH-Cu | 3.8 | 15.0 |
| 8.9 AH | 4.3 | 12.0 |

[a] Selectivities (wt%) were determined after 200 h on stream.

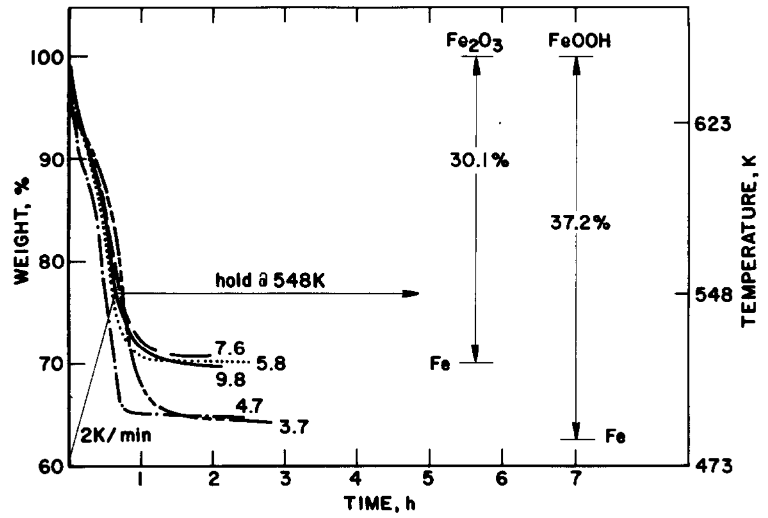

FIG. 5. Reduction of precipitated iron samples ($Na_2CO_3$) with $H_2$ from 473 to 548 K.

(without any prior reduction in $H_2$), more definitive data regarding the nature of these samples, both before and after activation, could be obtained using a two-step activation procedure. This procedure consisted of reduction in $H_2$, followed by carbiding with a mixture of 50% $H_2$ and 50% CO. The weight decreases in $H_2$ for samples prepared at high pH (Fig. 5) were nearly identical and corresponded closely to the weight loss calculated for reduction of $Fe_2O_3$ to metallic iron. The observed weight loss for catalysts prepared at low pH, however, was somewhat less than that calculated for the reduction of FeOOH to metallic iron, suggesting that these samples were a mixture of $Fe_2O_3$ and FeOOH. The presence of a significant amount of FeOOH in the samples prepared at low pH is also suggested by the rapid weight loss observed at low temperatures ($\alpha$-FeOOH decomposes slightly above 373 K).

When these reduced samples were carbided with synthesis gas, as shown in Fig. 6, a rapid weight gain was observed during the first 30 min, followed by a slow, steady increase. Although the weight increases observed for samples 3.7 SC and 4.7 SC were less than the increase calculated for conversion of metallic iron to $Fe_2C$, it is still possible that a portion of the weight increase was due to deposition of noncarbidic carbon-containing species on the surface. The large weight increases observed for samples 5.8 SC, 7.6 SC, and 9.8 SC were considerably in excess of the increase required for formation of $Fe_2C$ only, suggesting that this carbon deposition occurred to a greater extent on these samples.

Treatment of these carbided samples in $H_2$ in a temperature range from 548 to 628 K (2 K/min) resulted in a weight loss for samples 3.7 SC and 4.7 SC equivalent to the weight increase observed during the carbiding step, indicating that no inert graphitic carbon had formed. The weight loss resulting when samples 5.8 SC, 7.6 SC, and 9.8 SC were treated with $H_2$ was considerably less than the weight increase observed during carbiding. This indicated a significant amount of the weight increase probably was due to formation of a nonreactive graphitic carbon. It is possible, however, that at least a portion of this graphitic carbon was formed not during exposure to synthesis gas but during the helium flush at 548 K prior to exposure to $H_2$.

Reduction of the ammonium hydroxide-precipitated samples indicated that reduction was more rapid with sample 7.6 AH

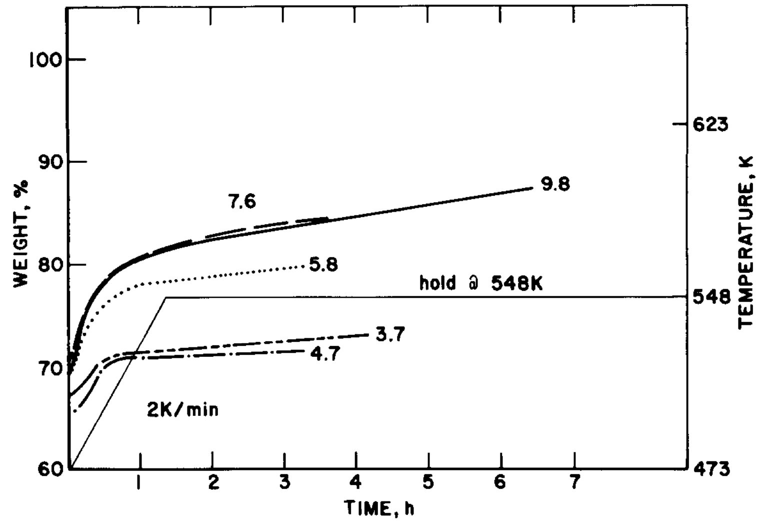

Fig. 6. Carbiding of reduced precipitated iron samples ($Na_2CO_3$) from 473 to 548 K with 50% $H_2$–50% CO.

(Fig. 7). The weight changes that occurred during carbiding of reduced $NH_4OH$-precipitated samples from 473 to 548 K (Fig. 8) indicated that substantially less carbon deposition took place on these samples compared to samples 5.8 SC, 7.6 SC, and 9.6 SC (Fig. 6).

DISCUSSION

It is apparent that the pH of precipitation affected not only the physical properties of the catalyst as reflected in the significantly different surface areas and pore volumes shown in Table 2, but also the chemical composition of the catalyst as indicated by the almost 10-fold variation in the Cu/Fe ratio and 15-fold variation in the Na/Fe ratio (Table 1). It is probable that when precipitated iron catalysts are prepared using the batchwise addition of an iron nitrate solution to a basic sodium carbonate solution (or vice versa), the manner of solution addi-

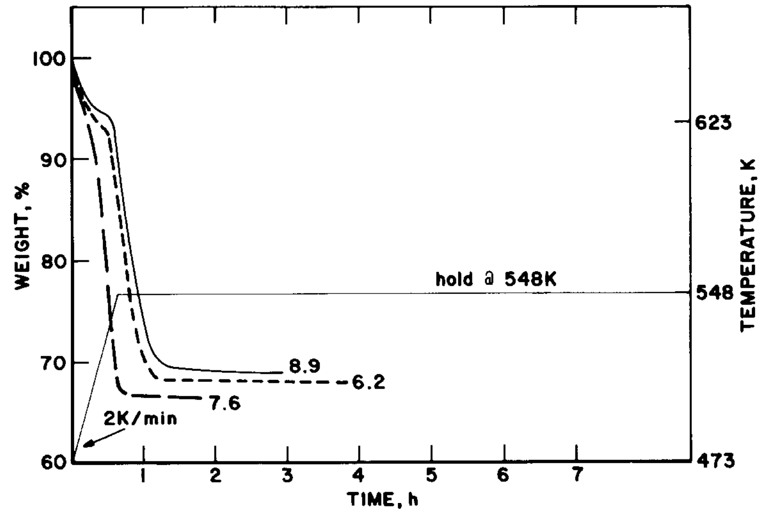

Fig. 7. Reduction of precipitated iron catalysts ($NH_4OH$) with $H_2$ from 473 to 548 K.

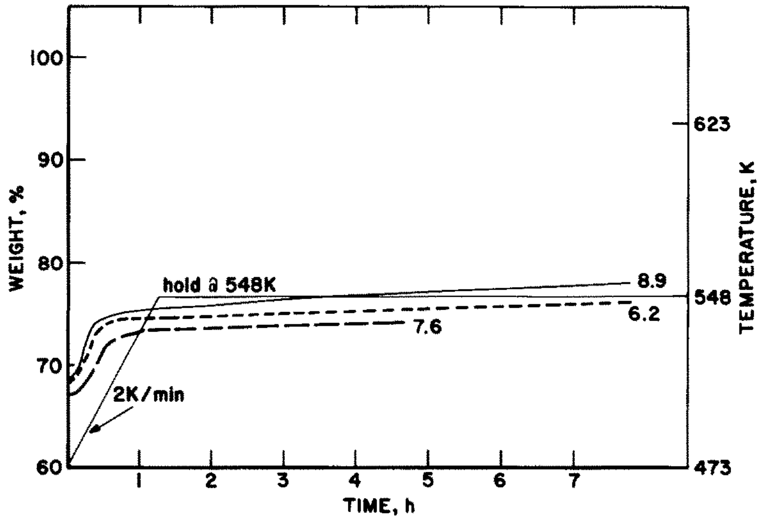

FIG. 8. Carbiding of reduced precipitated iron catalysts ($NH_4OH$) from 473 to 548 K with 50% $H_2$–50% CO.

tion is as important as the final pH of the catalyst slurry. For example, addition of a sodium carbonate solution to an iron nitrate plus copper nitrate solution would result in precipitation of little of the copper during the initial stages when the bulk of the iron is precipitated. The extent to which the copper would be precipitated would depend on the final pH of the slurry. Even if the final pH was sufficiently high to precipitate out all the copper, the degree of contact between the copper and iron would be minimal unless the precipitate was reslurried and mixed thoroughly. On the other hand, addition of an iron plus copper nitrate solution to a carbonate solution would result in complete precipitation of all the copper provided the final pH of the slurry was above 6. If the final pH was too low (3–4), then the copper precipitated initially might dissolve. An advantage of the Kölbel in-line mixing technique is the nearly simultaneous precipitation of the copper and iron (provided the pH is sufficiently high). When using sodium salts in batch preparations, the Na/Fe ratio should be low provided the sodium salt solution is added to the iron nitrate solution, and the final pH is less than 6. It is not clear from the present work how the Na/Fe ratio would be affected if the final pH was above 6. Likewise, if the iron nitrate solution was added to the sodium-containing solution, the Na/Fe ratio should be high if the final pH was above 6; if the final pH was less than 6, insufficient data are available to predict the Na/Fe ratio.

In the case of the $NH_4OH$-precipitated catalysts, even at a pH of 7.6, only 16% of the copper was precipitated. While the pH should be sufficiently high to precipitate out all the copper, the formation of a soluble copper–ammonia complex apparently results in incomplete precipitation of the copper.

Deactivation of the $Na_2CO_3$-precipitated catalysts prepared at high pH was severe during the first 200 h on stream, while the catalysts prepared at low pH declined in activity at a significantly lower rate. In contrast to the former, the activity of $NH_4OH$-precipitated catalysts decreased relatively slowly during the first 300 h on stream, followed by a gradual stabilization. The $NH_4OH$-precipitated catalysts showed a weight increase (Fig. 8) corresponding only to that expected for the formation of iron carbide ($Fe_2C$). Previous workers (*10*, *11*) have shown that the weight increase observed after hydrogenation of carbon monoxide over iron surfaces consists of at least three carbonaceous species—(1) graphitic carbon, (2) carbidic carbon, and (3) a $CH_x$ phase. These investigators found the latter two were reactive toward hydrogenation, whereas the graphitic carbon was inactive and believed to be responsible for the deactivation of the catalyst. These present studies are consistent with the thermogravimetric results showing all of the weight increase during the carbiding step with the catalysts prepared at low pH, which deactivated slowly, was due to reactive carbonaceous species removable by treatment in $H_2$. The low-stability catalysts prepared at high pH, however, underwent during carbiding a weight increase that must have included some nonreactive graphitic carbon because not all of the carbonaceous deposit could be removed by treatment in $H_2$.

The reasons for the substantial difference in the amount of carbonaceous deposits are not clear. The high bulk concentrations of sodium in the catalysts prepared at high pH, which exhibited the largest rates of weight increase during carbiding, suggest that sodium-containing species may be a factor. Doping of sample 4.7 SC with additional sodium (as $Na_2CO_3$) resulted in increased rates of carbon deposition. The $NH_4OH$-precipitated catalysts (0% Na) showed a weight increase corresponding only to that expected for formation of iron carbide ($Fe_2C$).

The increase in the olefin/paraffin ratio of the $C_2$–$C_4$ fraction, and the concomitant decrease in $C_1$–$C_4$ paraffins with decreasing pH for the $Na_2CO_3$-precipitated catalysts are of significant interest. Various investigators (*12–14*) have suggested that "aged surface carbon" may be partially responsible for extraneous methane formation. Surface science studies (*13, 15, 16*) indicate that $CH_x$-type intermediates gradually dehydrogenate and ultimately deteriorate into graphitic carbon, resulting in catalyst deactivation, as discussed earlier. Both activity and selectivity are possibly affected to some degree by the buildup of these carbonaceous deposits, since it has been shown these deposits can still produce methane provided they are not allowed to "age." While these carbonaceous deposits may account for the high methane selectivity, it still is not clear what factors are responsible for the high olefin selectivity. Jung *et al.* (*17*) have shown that high olefin selectivities are found for supported iron catalysts provided the crystallite size of the iron is sufficiently small. However, the crystallite size of these catalysts was smaller by at least a factor of 10 than those found for the precipitated iron catalysts. In addition, no significant change in crystallite size was observed as the pH of preparation varied, suggesting that the crystallite size was not a factor in the observed change in olefin selectivity.

The increase in olefin selectivity with decreasing soda content observed for the $Na_2CO_3$-precipitated samples was just the opposite of what most previous investigators have found (*18*). In addition, selectivity comparisons were made after 200 h; conversion levels at this time on stream were in fact somewhat higher for catalysts prepared at low pH, i.e., those catalysts having the highest olefin selectivity. Previous investigators (*17, 19*) have shown that the olefin selectivity depends on the percentage synthesis gas conversion, i.e., as synthesis gas conversion decreases, olefin selectivity increases. Thus, the high olefin selectivity observed for catalysts prepared at low pH, regardless of the low soda levels and high synthesis gas conversion, indicates that a still unidentified factor plays an important role in modifying catalyst behavior.

## CONCLUSIONS

Microreactor studies indicated that $Na_2CO_3$-precipitated catalysts prepared at low pH levels (<4.7) exhibited high olefin selectivity ($C_2$–$C_4$) and stability superior to that of catalysts prepared at high pH levels (>5.8). Catalysts prepared using ammonium hydroxide were the most stable (for up to 300 h), but the olefin selectivity was not as high as that found for catalysts prepared using $Na_2CO_3$. Graphitic carbon deposition occurred to a greater degree on $Na_2CO_3$-precipitated catalysts, especially those prepared at high pH. The high soda content of these catalysts was at least partially responsible for this deposition and presumably accounted for the higher rates of deactivation. Further studies are necessary to elucidate those factors responsible for the high olefin selectivity of the $Na_2CO_3$-precipitated catalysts.

## ACKNOWLEDGMENTS

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