Iron and Cobalt Fischer–Tropsch Catalysts Prepared by the Solvated Metal-Atom Technique

INTRODUCTION

Supported iron and cobalt catalysts, prepared by impregnation or precipitation methods, are not very active as Fischer–Tropsch catalysts when the metal loading is low. Depending on the support and its surface properties, the amount of metal loading necessary for an active catalyst may vary; however, supported cobalt catalysts with less than 5 wt% metal and iron catalysts with less than 20 wt% metal are fairly inactive as Fischer–Tropsch catalysts when prepared by conventional methods (1–3).

The poor catalytic activity at low metal loadings appears to be related to the interaction of metal oxides with the support and the influence of this interaction on the reducibility of the oxide. Metal cations may interact strongly with supports such as silica and alumina (4), forming silicates and aluminates (5) or other similar species (6), which are not as easily reducible as the bulk oxides. For example, cobalt, when deposited on silica by impregnation with an aqueous solution of cobalt nitrate, interacts with the hydroxyl groups of the silica, and after calcination forms a tetrahedral complex in which surface anions enter the coordination sphere (7). Similarly, cobalt supported on alumina may occupy tetrahedral lattice sites of the support where it is not easily reducible (6, 8, 9). At low metal loadings these sites are occupied preferentially so that the percentage of cobalt reducible to the metal decreases with decreasing metal loading (9). As the metal loading is increased a more easily reducible "bulk-like" phase forms on the surface of the catalyst, and the catalyst becomes increasingly active.

It is reasonable that at low metal loadings a more active catalyst would result from deposition on a support of a metal in the reduced, metallic state. Deposition of less than 5 wt% cobalt on alumina in the form of cobalt carbonyl produced catalysts of good activity (10). The Solvated Metal Atom Deposition Technique (SMAD) provides a method of catalyst preparation for which the deposition of metallic catalysts on a support has been demonstrated (11–13). This note reports a comparative study of the Fischer–Tropsch synthesis activity of iron and cobalt catalysts prepared by this technique and supported on silica with less than 5 wt% of the metal, and of analogous catalysts prepared by conventional impregnation techniques.

EXPERIMENTAL METHODS

The title catalysts were prepared by the solvated metal atom deposition technique described by Klabunde et al. (11–13) using a Ketjen silica as the support. The silica, with a pore volume of 1.06 cm³/g and a surface area of 59 m²/g, was dehydroxylated by calcining at 600°C before addition of the metal. Cobalt or iron metal was heated in a tantalum furnace and vaporized at 1400°C under vacuum and the metal vapor was cocondensed with toluene vapor at −196°C. The solid slurry of metal and toluene was slowly warmed and melted in the presence of the silica. After melting, the mixture was vigorously stirred and a metal–toluene/silica slurry was obtained. Once the metal had deposited on the silica, the excess toluene was removed by syringe and the metal/sil-

Total Surface Areas and CO Adsorption for the Control Catalysts and the Catalysts
Prepared by the SMAD Technique

Catalyst	Surface area (m²/g) (calcined at 500°C)	Surface area (m²/g) (reduced metal)	μCO adsorbed/ g catalyst
3.3% Fe/SiO₂ (Control)	53.5	56.3	—
4.5% Co/SiO₂ (Control)	50.6	53.4	4.5
3.3% Fe/SiO₂ (SMAD)	—	55.7	—
4.8% Co/SiO₂ (SMAD)	—	58.2	520

ica catalyst was vacuum-dried at room temperature for several hours at 10 Torr. The two catalysts prepared by this method contained 4.8 wt% Co and 3.3 wt% Fe, respectively; the metal contents were determined using X-ray fluorescence spectroscopy.

Two control catalysts were prepared by incipient wetness impregnation. Solutions of cobalt or iron nitrate (Mallinckrodt) were used for the impregnation. The catalysts were dried overnight at 110°C, and then calcined at 350°C for 1 h and overnight at 500°C. The compositions of the control catalysts were 4.5 wt% Co/SiO₂ and 3.3 wt% Fe/SiO₂. The catalytic tests were carried out in a fixed-bed, single-pass, flow-through system with a 1-in. i.d., stainless-steel reactor tube charged with 10 ml of the catalyst. Because the two SMAD catalysts were air sensitive, these catalysts were charged into the reactor tube in an argon atmosphere. The space above the catalyst was filled with quartz chips that acted as a preheater. Generally, the experiments were run for 28 h. Liquid and solid hydrocarbons and aqueous products were condensed out at −20°C and collected at the end of the test. The hydrocarbon products were analyzed on an HP5710A chromatograph with an OV-101 column while aqueous products were analyzed on an HP5750 chromatograph with a Porapak Q column. Gaseous products were analyzed periodically during

the tests on a Carle multicolumn chromatograph (Refinery Gas GC 111H, Series S).

All of the experiments with the cobalt catalysts were conducted at 230°C, 6 bar, a H₂:CO ratio of 2, and a space velocity of 720 GHSV and those with iron catalysts were conducted at 320°C, 11 bar, a H₂:CO ratio of 1, and a space velocity of 720 GHSV. Prior to the experiments, the impregnated and calcined control catalysts were pretreated for 17 h with hydrogen at 400°C. A second series of tests were also carried out after hydrogen pretreatment at 500°C. Three different experiments were made for the two SMAD catalysts. First, both catalysts were tested without pretreatment. Second, like the control catalysts, the iron SMAD catalyst was tested after a 17-h pretreatment with hydrogen at 500°C. Finally, both SMAD catalysts were tested after using the same calcination and reduction procedure applied to the control catalysts.

RESULTS AND DISCUSSION

The total surface areas and CO adsorption for the catalyst samples are shown in Table 1. The total surface areas were determined by a five-point BET method while the CO adsorptions were measured in a constant volume chemisorption apparatus. Prior to the adsorption measurements, the cobalt/silica control catalyst was reduced

TABLE 2

Synthesis Gas Catalytic Results for an Iron/Silica Catalyst Prepared
by the SMAD Technique

Pretreatment	None	Reduced at 500°C	Calcined and reduced at 500°C
% CO conversion to hydrocarbons and oxygenates	24	27	1
Distribution, carbon mole%			
CH_4	34	30	27
C_2–C_4 (total)	54	65	73
C_2–C_4 (olefins)	30	31	56
C_5^+	11	3	~0
Oxygenates	1	1	1
% C_2–C_4 olefins	56	48	77
α	0.67	0.64	—

Note. Catalyst—3.3% Fe/SiO$_2$ (320°C, 11 bar, H$_2$:CO = 1, 720 GHSV).

with hydrogen for 6 h at 500°C and then outgassed for 17 h at 250°C. The cobalt/silica SMAD catalyst received no prereduction, but was outgassed for 17 h at room temperature. The total surface areas are similar for all of the catalyst samples, although there is some indication that the surface area of the control catalysts increases after reduction. The chemisorption experiments show that the CO adsorption of the cobalt SMAD catalyst is two orders of magnitude higher than that of the cobalt control catalyst.

A summary of the synthesis gas experimental tests is given in Tables 2 and 3 for the iron and cobalt SMAD catalysts, respectively. As the tables illustrate, both the iron and the cobalt SMAD catalysts were active without hydrogen pretreatment. In contrast, the two control catalysts, prepared by incipient wetness impregnation and reduced at 400 or 500°C, were inactive. The selectivity of the active catalysts was not unusual, and the liquid products collected at the end of the experiments followed the Schulz–Flory polymeric distribution (14–16). The probability of chain growth for the liquid products is shown for

both catalysts in Tables 2 and 3. These probabilities were calculated using the equation reported by Henrici-Olive' and Olive' (16).

Reduction in hydrogen at 500°C of the iron SMAD catalyst had little effect on the activity of the catalyst, as shown in Table 2,

TABLE 3

Synthesis Gas Catalytic Results for a Cobalt/Silica
Catalyst Prepared by the SMAD Technique

Pretreatment	None	Calcined and reduced at 500°C
% CO conversion to hydrocarbons and oxygenates	31	3
Distribution, carbon mole%		
CH_4	22	27
C_2–C_4 (total)	20	22
C_2–C_4 (olefins)	6	6
C_5^+	55	51
Oxygenates	3	~0
% C_2–C_4 olefins	30	27
α	0.80	0.82

Note. Catalysts—4.8% Co/SiO$_2$ (230°C, 6 bar, H$_2$:CO = 2, 720 GHSV).

although there was an apparent shift in the product distribution to lower molecular weight products. During the hydrogen reduction, the catalyst was monitored for methane production which could result from the hydrogenation of carbonaceous material deposited on the catalyst during the preparation. Only trace amounts of methane were observed.

Calcination, followed by reduction in hydrogen at 500°C of the iron and cobalt SMAD catalysts lowered the conversion to hydrocarbon products by an order of magnitude; however, even this activity exceeded the activity of the standard impregnated catalysts. The selectivity of the cobalt catalyst was essentially unchanged by this treatment while that of the iron catalyst appeared to shift to lower molecular weight products. The conversion for the iron catalyst was so small, though, that collection of a significant amount of liquid phase product was not possible. Clearly, this would skew the apparent product distribution to lower molecular weight products.

CONCLUSIONS

The preparation of catalysts using the solvated metal atom deposition technique leads to considerably more active catalysts than catalysts with the same metal loading prepared by incipient impregnation. These catalysts show activity without hydrogen pretreatment and at metal loadings which are considered low for iron or cobalt Fischer–Tropsch catalysts. Calcining and reducing these catalysts in a manner similar to that used for the control catalysts result in catalysts of poor activity, but the selectivities are not noticeably affected by this treatment. The poor activity of the calcined and reduced control catalysts can be attributed to incomplete reduction or low metal surface area. The iron and cobalt oxide supported on silica may be in a form which is difficult to reduce, as suggested in the introduction. Alternatively, or additionally, the

calcination may cause a sintering of the catalyst to a lower metal surface area than the catalyst prepared by the solvated metal atom deposition technique.

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