**Title:** **PREPARATION OF FISCHER-TROPSCH CATALYSTS FROM COBALT/IRON HYDROTALCITES**

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## ABSTRACT

Compounds with the hydrotalcite structure (hydrotalcites) have properties that make them attractive as precursors for Fischer-Tropsch catalysts. A series of single-phase hydrotalcites with cobalt/iron atom ratios ranging from 75/25 to 25/75 has been synthesized. Mixed cobalt/iron oxides have been prepared from these hydrotalcites by controlled thermal decomposition. Thermal decomposition at temperatures below 600 °C typically produced a single-phase mixed metal oxide with a spinel structure. The BET surface areas of the spinel samples have been found to be as high as about 150 $m^2/g$. Appropriate reducing pretreatments have been developed for several of these spinels and their activity, selectivity, and activity and selectivity maintenance have been examined at 13 MPa in a fixed-bed microreactor.

## OBJECTIVES

The immediate objectives are to explore the catalytic properties of Fischer-Tropsch (FT) catalysts prepared from hydrotalcites and to understand the structure underlying these properties. The ultimate objective is to prepare FT catalysts with adequate activity, selectivity, and longevity for bubble column reactors.

## APPROACHES

*Introduction*

Mixed metal oxides are important in many catalytic applications, both as catalysts and supports. The precursors used in the syntheses of mixed metal oxides are known to influence the physical and chemical properties of the resulting mixed metal oxides. Precursors commonly used for the preparation of these oxides include mixed metal hydroxides and carbonates coprecipitated from basic solution. Materials with a hydrotalcite-like structure, commonly referred to as hydrotalcites after one of the best known minerals of this structural group, have received much attention recently as precursors for catalytic applications. Examples include catalysts for methanol synthesis containing Cu, Zn, Cr, and Al (1,2,3) and catalysts for FT synthesis containing Co, Cu, Zn, and Cr(4).

Hydrotalcites have a layered structure similar to clays. The structure, illustrated in Figure 1, resembles that of the mineral brucite, $Mg(OH)_2$. It consists of stacks of brucite-like metal hydroxide sheets in which substitution of trivalent metal cations for divalent metal cations within the sheets results in a net positive charge. The positive charge is balanced in the structure by an additional layer of hydrated anions between the brucite-like sheets. A generalized formula for hydrotalcite-like compounds can be

written as:

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}A_{x/n}^{n-}\cdot zH_2O$$

where $M^{2+}$ and $M^{3+}$ can be a variety of metals with appropriate ionic radii. The charge compensating anion is also variable with the ionic radius of the charge compensating anion being of only minor importance because the layer separation can adjust to accommodate size differences. Examples are as follows:

$M^{2+}$ = Mg, Ni, Zn, Co, Fe, Cu, etc.

$M^{3+}$ = Al, Cr, Fe, etc.

A = $CO_3$, OH, $SO_4$, $CrO_4$, $V_{10}O_{28}$, etc.

There are many naturally occurring minerals having this structure. These minerals typically have the ideal stoichiometry:

$$M_6^{2+}M_2^{3+}(OH)_{16}CO_3\cdot 4H_2O$$

Compounds with the hydrotalcite structure have several characteristics that make them valuable as precursors for FT catalysts. Among these is the ability of the structure to accommodate a variety of potentially useful transition metals in a single lattice and the ability to control the synthesis conditions to yield a high surface area material upon decomposition to a spinel phase. Furthermore, Co-containing and Fe-containing spinel phases have shown good activity and selectivity for FT synthesis and, when judiciously prepared and pretreated, have the potential for the physical stability required of a slurry FT catalyst.

This research examines the potential of hydrotalcites as precursors for the preparation of slurry Co/Fe FT catalysts. We report results from the initial phase of this work, the preparation of Co/Fe hydrotalcite samples and their thermal decomposition to spinel phases of intermediate-to-high surface area. We also report the initial results of studies defining appropriate reducing pretreatments for the spinels and their subsequent FT activity and selectivity in a fixed-bed microreactor. Finally, addition of promoters will likely be needed to improve various properties of the catalyst. We therefore report synthesis and thermal decomposition of Co/Fe hydrotalcites also containing typical FT catalyst promoters such as Cu or Al, as well as TPR results of some of these samples.

*Experimental*

The hydrotalcites in this study were prepared by a precipitation in base of the appropriate metal salts. The specific conditions used for the syntheses were varied to yield single-phase, well-crystallized hydrotalcites when possible. An aqueous solution of metal salts was prepared that contained the required ratio of metals for the target hydrotalcite, typically with a total metal concentration of about 0.5 M. The metal salt solution was added dropwise to an aqueous base that typically had an initial concentration of about 1 M. Concentrations were varied for some experiments. Potassium bases were used in most experiments because potassium is typically used to promote iron FT catalysts and additional potassium will be impregnated in many of these spinel samples before their use as catalysts. Thus, trace amounts of potassium retained in a hydrotalcite precursor are less likely to affect the

behavior of the catalyst than are trace amounts of sodium from sodium bases. Additions were usually done at 25°C with magnetic stirring. The pH was monitored during the syntheses. Usually, at the end of the addition, the temperature of the slurry was increased to about 60°C. The slurry was aged, typically for 18 hours, at elevated temperature to promote hydrotalcite formation. After the aging period the product was isolated by filtration, washed, and dried at 50°C. Hydrotalcites were thermally decomposed in air at various temperatures between 125 and 1000°C, usually for 2.5 hours, to determine what mixed metal oxide(s) would be formed.

The phases resulting from the hydrotalcite syntheses and the thermal decompositions were determined by means of x-ray diffraction (XRD). Chemical analyses for K, Na, Al, Co, Fe and Cl in these samples were requested but results were not available when this report was written. Morphologies of these materials were studied with scanning electron microscopy (SEM). Surface areas of the mixed oxides were measured by application of the BET method to $N_2$ physisorption isotherms. The reduction characteristics of the mixed metal oxides were investigated by means of temperature programmed reduction (TPR) with 10% $H_2$ in argon, 10% CO in helium, or 5% $H_2$ / 5% CO in argon. For each TPR experiment, approximately 50 mg of spinel was loaded in a quartz U-tube mounted in an Altamira Instruments AMI-1 unit. Each sample was typically heated at 5 °C $min^{-1}$ in a total gas flow rate of 60 sccm. An Ametek mass spectrometer was used for gas analysis. Catalytic reaction studies were done with 0.3-1.5 g of sample loaded in a fixed-bed stainless steel reactor. The wax product was collected in a hot trap operated at 150 °C, liquid aqueous and oil products were collected in a cold trap operated at 20 °C, and the outlet gas stream was analyzed on-line with a Hewlett-Packard 5730 gas chromatograph.

*Results and Discussion- Fe/Co*

A stepwise strategy was used to develop the hydrotalcite syntheses. First, the hydrotalcite compositional range attainable for Co (II) with Fe (III) was determined. Then, the use of Fe (II) to increase the iron content of the hydrotalcite lattice was investigated.

Cobalt (II) nitrate and iron (III) nitrate were used as starting materials for the first part of the synthesis study. Potassium bicarbonate solution at an initial concentration of 1.25 M was used as the base. Hydrotalcite formation with Co (II) to Fe(III) atom ratios ranging from 80/20 to 25/75 was attempted in this series of experiments. The results are shown in Table 1. With this method well-crystallized, single-phase hydrotalcites could be prepared with Co (II) to Fe (III) atom ratios from 75/25 to 50/50. At lower cobalt contents some poorly crystallized iron (III) hydroxide was produced along with hydrotalcite and, at higher cobalt contents, some cobalt carbonate was produced. The starting pH for a synthesis was about 8. During the addition of metal salt solution, the pH typically dropped below 7 and a pinkish-tan slurry formed. As the slurry was aged and heated to 60°C, the pH rose to about 9 accompanied by a change in color to a darker reddish-brown, usually indicating formation of the hydrotalcite.

A number of experiments were conducted in an attempt to increase the iron content of the hydrotalcite lattice. Table 2 outlines several of the more successful experiments and the resulting compounds. In all experiments in this series metal chloride salts were used instead of the nitrate salts in order to inhibit the rate of $Fe^{2+}$ oxidation in solution. Several of the syntheses were based on the work reported by Uzunova *et al.* (5). The $M^{3+}$ required for a stable hydrotalcite lattice was provided by the oxidation of

some of the Fe (II) to Fe (III) through contact with atmospheric oxygen during the synthesis. The result of this set of experiments was the extension of the hydrotalcite cobalt to iron ratio to 25/75.

Figure 2 shows XRD patterns for Fe/Co hydrotalcites prepared by the two methods. A peak due to a $CoCO_3$ impurity is visible just above $2\Theta = 30°$ in the pattern for 75Co25Fe hydrotalcite. The large shoulders near the first two peaks in the pattern for 33Co67Fe are likely due to the lack of uniformity in the stacking pattern of the layers. The peaks are noticeably broader for the 25Co75Fe hydrotalcite, indicating smaller crystallite sizes.

The thermal decomposition behavior of several Co/Fe hydrotalcites was examined. The most extensive decomposition study was done for an intermediate composition hydrotalcite with an atom ratio of 67Co to 33Fe, which was decomposed in air at temperatures between 125 °C and 1000 °C. The samples were heated quickly by placing them in a muffle furnace that was already at the desired decomposition temperature and holding them at temperature for 2.5 hours. The results are shown in Table 3. It was found that a spinel phase, referred to as spinel A, was the only crystalline compound present following decomposition at temperatures of 200 to 600°C. Decomposition at 700°C produced a second spinel, spinel B, which was the dominant phase after decomposition at 800°C. Decomposition at 900°C yielded only spinel B, and decomposition above 1000°C began to decompose spinel B to cobalt oxides. The surface areas for these samples decreased from 153 to 18 $m^2/g$ as decomposition temperature increased from 300 °C to 700 °C. This loss of surface area was probably due to a loss of internal particle porosity because no evidence for sintering or for other changes in particle morphology was apparent in SEM. Hydrotalcites with other Co to Fe ratios showed similar behavior. However, for some high iron hydrotalcites two spinels were always present after decomposition. It was also found that slower heating of a sample to the decomposition temperature influenced the relative amounts of the spinels formed.

Table 4 shows the BET surface areas for spinels resulting from decomposition of Fe/Co hydrotalcites at 500 and 600 °C. Decomposition at the lower temperature (500 °C) produced higher surface area materials, as shown previously for the 67Co33Fe spinels. It also appears that the iron-rich spinels, 33Co67Fe and 25Co75Fe, had higher surface areas than spinels of intermediate or cobalt-rich composition. The higher surface area is consistent with the smaller crystallite sizes seen for the parent hydrotalcites in Figure 2. The higher surface area likely reflects the different preparation method used for synthesis of these materials and does not imply any inherent difference in the surface area of iron-rich Co/Fe spinels.

Conditions for the reducing pretreatment needed to convert spinel samples to FT catalysts were investigated. Figure 3 shows the TPR of the 25Co75Fe spinel in 10%CO/He. The major feature is a CO uptake peak occurring slightly above 300 °C. This likely represents reduction and carbiding of the spinel. The decrease in the m/z = 28 signal at temperatures above ~340 °C likely reflects deposition of surface carbon on the catalyst rather than any further reduction of the bulk oxide. A fresh spinel sample was given an isothermal treatment resembling the conditions of this TPR peak. This was done at 260 °C in pure flowing CO for 20 h. This treatment produced a material consisting of several carbide and metallic phases and no oxide phases; the XRD pattern showed two clear patterns of phases that are isostuctural with $\alpha$-Fe and with iron $\chi$-carbide. The relative amounts of the constituent phases and their exact compositions have not yet been determined. This CO-treated material had a BET surface area of 59 $m^2\ g^{-1}$, similar to that of the parent spinel.

Table 5 summarizes the results of FT synthesis with the 25Co75Fe spinel given the isothermal CO treatment as a pretreatment. The yield of light hydrocarbon ($C_1$-$C_5$) synthesis measured after 28.8 h is typical for FT catalysts under these conditions. This yield decayed 30% after an additional day on stream. A great deal of free carbon accumulated on the catalyst during these 49.5 h of synthesis, consistent with deactivation due to excess surface carbon deposition. The $H_2$/CO usage ratio seen after 28.8 h of synthesis was higher than would be expected for a typical Fe FT catalyst; the water-gas shift reaction is far from equilibrium even at the reactor outlet.

The last row in Table 5 shows the yield of CO conversion to all products except $H_2O$ and $CO_2$. This value is the integrated yield calculated from each on-line gas analysis and from analysis of the oil and wax fractions obtained for the entire 49.5 h of experiment. Figure 4 shows the overall carbon number distribution ("Anderson-Schulz-Flory" plot) for these integrated data. Gas make ($C_1$-$C_5$) approached 30% of the product, corresponding to a low "$\alpha$" value. The probability of carbon chain growth did increase for heavier carbon numbers; a linear regression of the $C_{20}$-$C_{35}$ fraction gave $\alpha = 0.82$. The oil product (not shown in tables or figures) was over 50% olefins and 14% alcohols.

*Results And Discussion- Addition of Cu and Al modifiers*

Copper (II) addition to the hydrotalcite lattice was initially attempted by substituting copper (II) nitrate for part of the cobalt (II) nitrate using the same synthesis method. (Copper is frequently added to precipitated iron catalysts to facilitate reduction.) The atom ratio was 20 Cu(II) / 40 Co(II) / 40 Fe(III). The % Cu was much higher than typically used for FT promotion, and was used so that any undesired phases produced during the synthesis could be detected and identified by XRD. The initial synthesis attempt resulted in primarily hydrotalcite with a trace of malachite, $Cu_2CO_3(OH)_2$. Lowering the base concentration from 1.25 M to 1.0 M eliminated the malachite contamination of the single phase hydrotalcite. Similar results have been obtained with Fe-rich hydrotalcites prepared with solutions of Co(II)/Fe(II)/Fe(III) chlorides; up to 12 metal% Cu has been added to the hydrotalcite lattice under these conditions. Copper can therefore be introduced into the Co/Fe hydrotalcite lattice in concentrations much higher than have typically been needed in FT catalysis.

Other results have shown the feasibility of Al substitution in the Co/Fe hydrotalcite lattice. Hydrotalcites with compositions of 75Co25Al and 75Co20Fe5Al were prepared and thermally decomposed. Table 6 shows BET surface areas of 75Co(25-x)Fe(x)Al spinels. Although Al substitution to the lattice increased the surface area, thermal decomposition still yielded a spinel powder that was coarser than the relatively fine 75Co25Fe spinel.

TPR studies with 10% $H_2$/ Ar were done on each of the samples listed in Table 6. Figure 5 shows the results. The 75Co25Al sample required temperatures well above 600 °C for thorough reduction, in contrast to the 75Co25Fe spinel, which was completely reduced at 430 °C. The intermediate composition, 75Co20Fe5Al, showed intermediate behavior, requiring temperatures of at least 500 °C for nearly complete reduction.

**PLANS**

The major portion of hydrotalcite synthesis is complete. The focus of this work has shifted to catalytic reaction of pretreated spinels and to characterization of these catalysts.

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**Table 1. Results of Co(II)/Fe(III) hydrotalcite preparations using metal nitrates**

| Co (II) | Fe (III) | Resulting Phases |
|---|---|---|
| 80 | 20 | HTC + trace $CoCO_3$ + trace unidentified |
| 75 | 25 | HTC + trace $CoCO_3$ |
| 67 | 33 | HTC |
| 50 | 50 | HTC |
| 33 | 67 | HTC + minor $Fe(OH)_3$ |
| 25 | 75 | HTC + $Fe(OH)_3$ |

HTC = hydrotalcite

**Table 2. Use of Fe(II) to increase iron content of hydrotalcite prepared with metal chlorides**

| Co (II) | Fe (II) | Base | Start pH | Result |
|---|---|---|---|---|
| 25 | 75 | $KHCO_3$ | 8.0 | HTC + trace $Fe(OH)_3$ |
| 25 | 75 | $KHCO_3 + K_2CO_3$ | 8.9 | Goethite + $CoCO_3$ |
| 33 | 67 | $KOH + K_2CO_3$ | 12.8 | HTC |
| 25 | 75 | $KOH + K_2CO_3$ | 12.8 | HTC |

HTC = hydrotalcite

**Table 3. Thermal decomposition of 67Co33Fe hydrotalcite**

| Temperature (°C) | Phase | Surface area $m^2/g$ |
|---|---|---|
| 50 | HTC | - |
| 125 | HTC + amorph | - |
| 200 | Spinel A | - |
| 300 | Spinel A | 153 |
| 400 | Spinel A | 95 |
| 500 | Spinel A | 57 |
| 600 | Spinel A | 29 |
| 700 | Spinel A + B | 18 |
| 800 | Spinel A + B | - |
| 900 | Spinel B | - |
| 1000 | Spinel B + CoO + $Co_3O_4$ | - |

**Table 4. Surface areas of Co/Fe spinels**

| Co | Fe | Other | BET Surface area ($m^2.g^{-1}$), for samples decomposed at: 500 °C | 600 °C |
|---|---|---|---|---|
| 100 | --- | --- | --- | --- |
| 75 | 25 | --- | 52 | 30 |
| 67 | 33 | --- | 57 | 29 |
| 50 | 50 | --- | --- | 34 |
| 33 | 67 | --- | --- | 47 |
| 25 | 75 | --- | 76 | --- |
| 25 | 75 | K* | 60 | --- |

* Spinel impregnated with 3.0% $K_2CO_3$

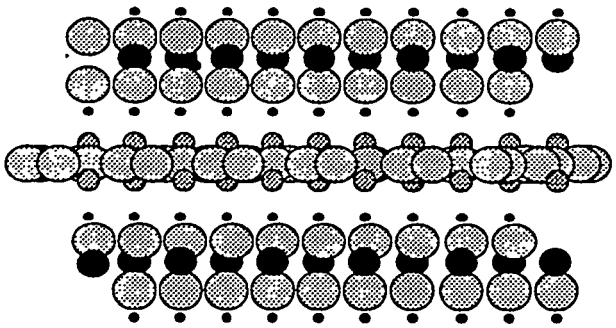
**Table 5. Fischer-Tropsch synthesis with 25Co75Fe spinel***

| | | |
|---|---|---|
| Time (h) | 28.8 | 49.5 |
| Conversions (%) | | |
| $H_2$ | ~27 | --- |
| CO | ~15 | --- |
| $H_2$/CO usage ratio | ~1.2 | --- |
| Space-time yield of $C_1$-$C_5$ (g / kg / h) | 106 | 73 |
| Space-time yield, CO converted to organic products (g CO / kg / h) | 313 | |

* Pretreatment conditions: CO, 20 h, 3.35 WHSV, 260 °C, 0.13 MPa
Reaction conditions 0.71 H2/CO, 3.52 WHSV, 260 °C, 1.32 MPa

**Table 6. Surface areas of Co/Fe/Al Spinels**

| | | | BET Surface Area ($m^2 g^{-1}$), samples decomposed at: | |
|---|---|---|---|---|
| Co | Fe | Al | 500 °C | 600 °C |
| 75 | 25 | --- | 52 | 30 |
| 75 | --- | 25 | 81 | --- |
| 75 | 20 | 5 | 66 | --- |




$$[M^{2+}_{1-x} M^{3+}_{x} (OH)_2] A^{n-}_{x/n} \cdot mH_2O$$

$M^{2+}$ = Mg, Zn, Ni, Co, Mn, Cu, ....

$M^{3+}$ = Al, Fe, Cr, Mn, Co, ....

A = $CO_3^{2-}$, $SO_4^{2-}$, $OH^-$, ...

◆ **Example:** $Mg_6 Al_2 (OH)_{16} CO_3 \cdot H_2O$ (Hydrotalcite)

Figure 1. Layered structure of the hydrotalcite-like compounds

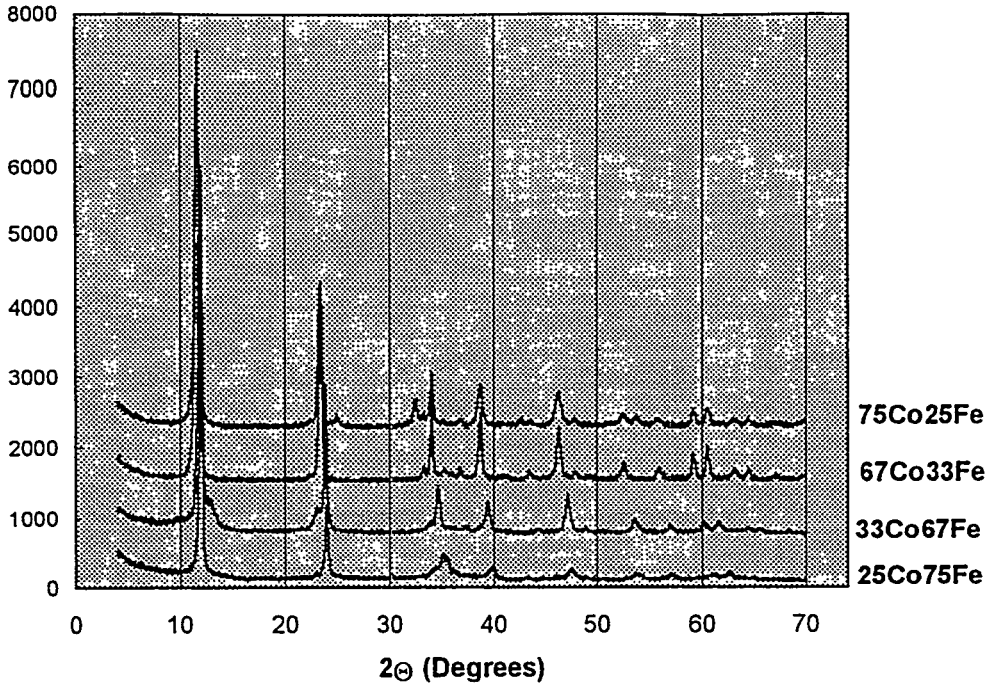



Figure 2. X-ray diffraction patterns of Co/Fe hydrotalcites

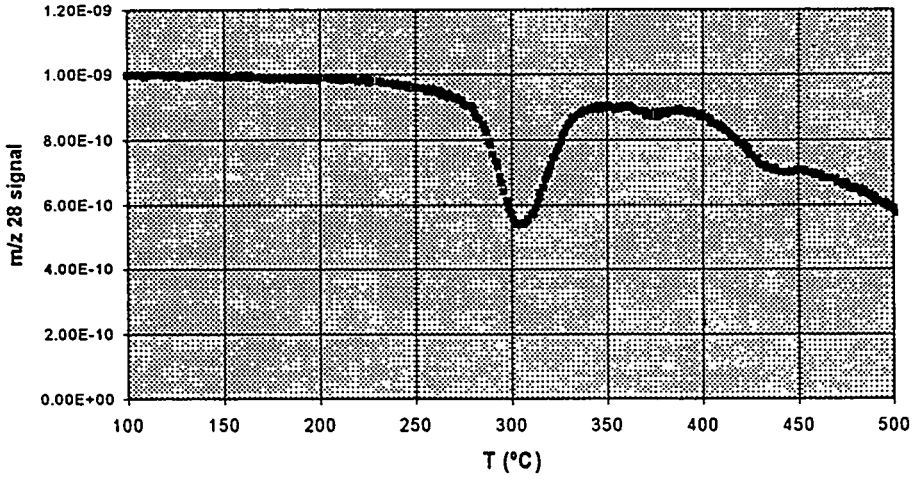



Figure 3. Temperature-programmed reduction of 25Co75Fe spinel in 10% CO/ He at a heating rate of 5 °C $min^{-1}$

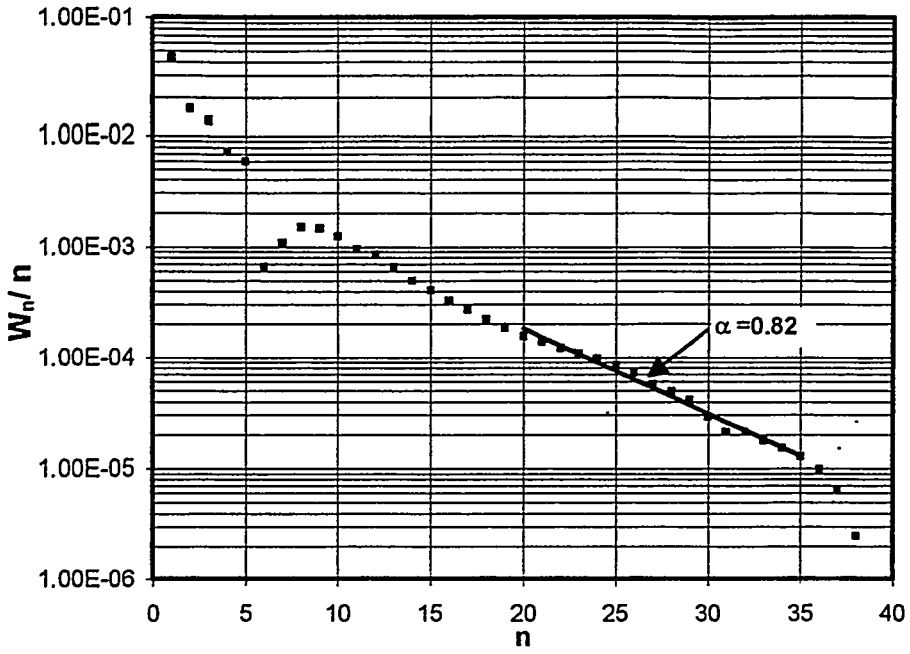



Figure 4. Distribution of carbon chain lengths ("Anderson-Schulz-Flory" plot), 25Co75Fe. (The discontinuity for $C_6$-$C_8$ reflects the fact that on-line gas analysis was not made for these products.)

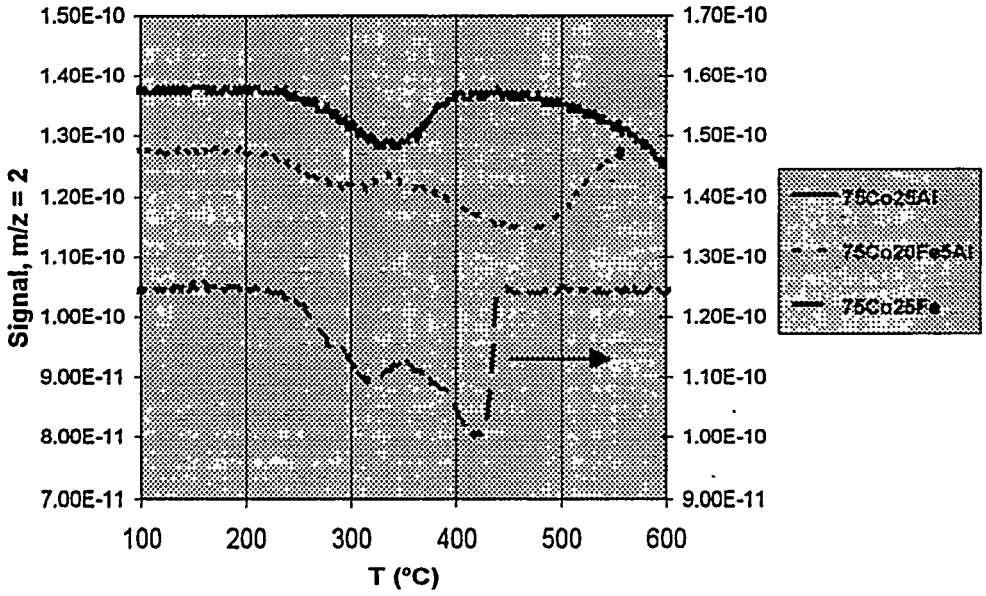



Figure 5. Temperature-programmed reduction of Co/Fe/Al spinels in 10% $H_2$/Ar at a heating rate of 5 °C $min^{-1}$