Zeolite-Supported Metal Catalysts for Fischer–Tropsch Reactions

I. A New Preparation Method

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A new preparation method of zeolite-supported metal catalysts is described. The method is based on the reaction between a metal-exchanged zeolite and an anionic, metal-containing coordination compound, specifically a water-soluble, metal cyanide complex. The reaction product is an insoluble compound distributed throughout the zeolite. Subsequent reduction in hydrogen results in finely dispersed metal in the zeolite. The method described can be used in the preparation of single or polymetallic catalysts. A single metal catalyst is obtained when the metal in the exchanged zeolite is the same as the one in the coordination compound. If the metals are different, a bimetallic catalyst will result. The method can be used for the preparation of a variety of zeolite-supported metal catalysts. In this paper the preparation of catalysts to be used in Fischer–Tropsch reactions is described. The materials prepared have been characterized by infrared and TGA/DTA methods.

INTRODUCTION

The increasing demand for energy has renewed interest in the catalytic synthesis of hydrocarbons from CO and H_2 mixtures by the so-called Fischer–Tropsch reaction. A variety of supported Fischer–Tropsch catalysts have been investigated in recent years (*1–6*).

While silica, alumina, and other metal oxides have been widely used as metal supports for Fischer–Tropsch catalysts, the use of zeolite supports has been fairly limited. For example, Ballivet-Tkatchenko *et al.* (*7, 8*) have prepared such catalysts by adsorbing iron carbonyl into a faujasite-type HY zeolite. The utilization of ZSM-5 zeolites in Fischer–Tropsch catalysis has recently been investigated (*9–11*). The use of iron supported on silicalite for the conversion of H_2–CO mixtures to hydrocarbons has also been described (*11*). Elliott and Lunsford (*12*) have investigated the use of zeolite-supported metal clusters in the catalytic hydrogenation of CO.

Due to their shape-selective character, high surface area, acidic nature, and well-defined structure, zeolites can play an important role in Fischer–Tropsch catalysis. The high surface area allows a high degree of metal dispersion in the zeolite, while the acidity and shape-selectivity can significantly affect the selectivity of the catalyst.

Most metal/zeolite catalysts have been prepared by impregnation (*9, 11*), by ion exchange (*12–14*), or by adsorption of volatile metal compounds in the zeolitic cavities (*7*), followed by reduction under hydrogen or thermal decomposition. However, the use of these methods does not always lead to a uniform distribution of the metals on the support. Furthermore, in some instances it is difficult to reduce the metal cation in the exchanged zeolite to the elementary state in flowing hydrogen (e.g., iron in Fe^{2+}–Y zeolites) (*14, 15*).

We have developed a new method of preparing zeolite-supported metal catalysts, which provides a uniform distribution and a high degree of metal dispersion throughout the zeolite. The method is based on the reaction of a metal-exchanged zeolite with a metal-containing coordina-

tion compound, resulting in an insoluble compound distributed throughout the zeolite.

In this paper, the preparation method described is illustrated by using transition metal cyanide complexes in the reaction with metal-exchanged zeolites. For example, to prepare a zeolite-supported iron catalyst (iron/zeolite catalyst), the following reaction is used:

$$Fe^{2+}-Z + (NH_4)_3[Fe(CN)_6] \rightarrow$$
$$NH_4-Z + Fe_3[Fe(CN)_6]_2$$

and/or

$$[NH_4,Fe]-Z + Fe,NH_4[Fe(CN)_6]$$
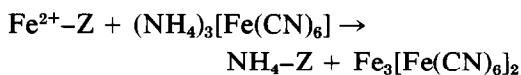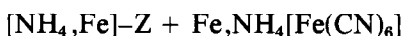
where Z is a zeolite. The composition of the resulting product depends upon reaction conditions. Subsequent reduction in hydrogen results in finely dispersed iron in the zeolite, while the zeolite itself is converted to the hydrogen form.

The same method can be used for the preparation of bimetallic or polymetallic catalysts. In this case, the metal-exchanged zeolite is reacted with a coordination compound containing a different metal atom in the anionic complex. Again using a cyanide complex as an example, an iron, cobalt/zeolite catalyst can be prepared by reacting Co–Z with $(NH_4)_4[Fe(CN)_6]$. The following reaction takes place:

$$Co^{2+}-Z + (NH_4)_4[Fe(CN)_6] \rightarrow$$
$$NH_4-Z + Co_2[Fe(CN)_6]$$

and/or

$$[NH_4,Co]-Z + Co(NH_4)_2[Fe(CN)_6]$$
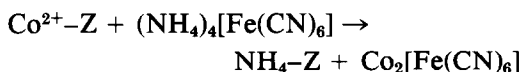
Subsequent reduction under hydrogen results in a zeolite containing dispersed iron and cobalt. This type of catalyst can also be prepared by reacting Fe–Z with $[Co(CN)_6]^{3-}$ ions.

In some instances the second metal can be introduced into the zeolite in cationic form. For example, catalysts frequently used in Fischer–Tropsch reactions contain iron and potassium. Such a catalyst can

be prepared by reacting Fe–Z with $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ and reducing the product in hydrogen.

EXPERIMENTAL

A. Catalyst Preparation

A faujasite-type zeolite (type Y) was used in these preparations, usually in the ammonium form. Water-soluble metal cyanide complexes were used in the reaction.

1. Iron/Y catalyst. A NaY zeolite, having SiO_2/Al_2O_3 ratio of 5.0, was consecutively exchanged with fresh portions of a 10% ammonium sulfate solution, until the resulting NH_4-Y zeolite contained less than 1% Na_2O.

NH_4Y zeolite (100 g) was reacted with a 10% ferrous sulfate solution for 3 hr at room temperature, under nitrogen. The resulting Fe,NH_4-Y zeolite was filtered, washed, and vacuum-dried at 65°C for 2 hr. The zeolite contained 3.9% Fe (dry basis).

Fe,NH_4-Y zeolite (50 g) was reacted with 500 ml of solution containing 7 g of $(NH_4)_4[Fe(CN)_6] \cdot H_2O$, under nitrogen. The product was filtered, washed, and vacuum-dried at 65°C for 2 hr. This material contained 4.65% Fe and had a surface area of 479 m^2/g.

Calcination in flowing hydrogen at 400°C for 4 hr results in a black product, containing finely dispersed iron. The gaseous products resulting from the reduction process were passed through a solution of caustic, to trap any volatile cyanide compound.

2. Iron, potassium/Y catalyst. Fe,NH_4-Y (100 g), prepared as described, was treated with 500 ml of a 7% solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ for 4 hr at room temperature under nitrogen. The product was filtered, washed, and dried at 65°C under vacuum. It was then reduced at 400°C for 4 hr under flowing hydrogen. The reduced, black material contained 4.5% Fe and 7.4% K_2O. It had a surface area of 512 m^2/g.

3. Iron, cobalt/Y catalyst. A Co,NH_4-Y zeolite was prepared by reacting NH_4Y with a cobalt nitrate solution, using a ratio

of 1 part zeolite to 1 part cobalt nitrate to 10 parts of water. The exchange was carried out at 90°C for 1 hr, with stirring. The exchanged zeolite was filtered, washed, and dried at 105°C for 2 hr. The zeolite contained 5.8% Co.

Co,NH$_4$–Y (100 g) was slurried in 500 ml of water. The slurry was mixed with 500 ml of a1 solution containing 36 g of (NH$_4$)$_4$[Fe(CN)$_6$] · H$_2$O. The reaction was carried out for 4 hr at room temperature, with stirring. The mauve product was filtered, washed, dried, and reduced at 400°C for 4 hr in flowing hydrogen. The reduced, black product contained 4.0% Co and 3.0% Fe. The surface area was 510 m^2/g.

4. Iron, cobalt, potassium/Y catalyst. This example illustrates the utilization of ferricyanide ions in the preparation process of a polymetallic catalyst. Co,NH$_4$–Y (100 g) was reacted with 600 ml of a solution containing 20 g K$_3$[Fe(CN)$_6$]. The reaction was carried out for 1 hr at room temperature, with stirring. The pink material was filtered, washed, and vacuum-dried at 65°C for 1 hr. The reduced material contained 3.3% Co, 2.0% Fe, and 5.4% K$_2$O. The surface area was 506 m^2/g.

5. Cobalt, iron, potassium/Y catalyst. Fe,NH$_4$–Y zeolite (100 g) was reacted with 500 ml of solution containing 20 g of K$_3$[Co(CN)$_6$]. The reaction was carried out under nitrogen for 1 hr at room temperature. The pale yellow product was filtered, washed, and dried at 65°C for 1 hr under vacuum. The dry material was reduced in flowing hydrogen at 400°C for 4 hr. The reduced, dark gray product contained 3.4% Fe, 1.6% Co, and 3.9% K$_2$O. The surface area was 566 m^2/g.

6. Iron, nickel/catalyst. A Ni,NH$_4$–Y zeolite was prepared by reacting NH$_4$Y with a solution of nickel nitrate using a ratio of 1 part zeolite to 1 part nickel nitrate to 10 parts of water. The reaction was carried out at 90°C for 1 hr. The green product was filtered, washed, and dried at 105°C for 2 hr. It contained 5.3% Ni (dry basis).

Ni,NH$_4$–Y (100 g) was reacted with (NH$_4$)$_4$[Fe(CN)$_6$] · H$_2$O under the same conditions as described for catalyst 3. The green product was filtered, washed, dried, and reduced in flowing hydrogen. The reduced black product contained 4.0% Fe and 4.4% Ni. The surface area was 515 m^2/g.

7. Iron, copper, sodium/Y catalyst. This example illustrates the use of [Fe(CN)$_5$NO]$^{2-}$ ions in the preparation of catalysts. A Cu,NH$_4$–Y zeolite was prepared by reacting an NH$_4$Y zeolite with a 10% copper nitrate solution at 90°C for 1 hr, using 5 ml solution for each gram of zeolite. The exchanged, oven-dried zeolite was reacted with a 10% Na$_2$[Fe(CN)$_5$NO] · 2H$_2$O solution, using 3.3 ml solution for each gram of zeolite. The reaction was carried out for 6 hr at room temperature. The light-green product was washed, dried, and reduced in flowing hydrogen. The reduced catalyst contained 4.3% Fe, 6.2% Cu, and 4.6% Na$_2$O. The surface area was 584 m^2/g.

8. Cobalt, copper, potassium/Y catalyst. A Cu,NH$_4$–Y zeolite was reacted with a 10% K$_3$[Co(CN)$_6$] solution for 6 hr at room temperature, using 3.6 ml of solution for each gram of zeolite. The light-blue product was filtered, washed, oven-dried, and reduced in flowing hydrogen. The reduced catalyst contained 3.6% Co, 5.5% Cu, and 9.9% K$_2$O. The surface area was 526 m^2/g.

Numerous other mono- or polymetallic catalysts can be prepared using procedures similar to those described. Any complex metal cyanide capable to form an insoluble compound with the zeolitic cation can be used in this procedure. Evidently, other factors like zeolite pore opening, diffusivity, accessibility of zeolitic cations, etc. will affect the nature of the reaction product and the metal distribution in the catalyst.

B. Catalyst Characterization: Instrumentation and Techniques

The infrared spectra were obtained with a Beckman 4260 ir spectrophotometer connected to a Wang 2200 computer system

with disc drive and printer. The spectra were recorded for the region 300–2600 cm^{-1}, using the KBr pellet technique. This frequency region covered the zeolite framework vibrations as well as CN, NH, and H_2O vibrations. The spectra of samples containing complex cyanides were obtained after drying the material at 65°C for 2 hr under vacuum. The reduced catalysts were submitted to no further treatment prior to ir measurements.

The X-ray diffractograms were obtained on a Norelco X-ray diffractometer from Philips. The surface area was measured on a Micromeritics 2200 unit, using the BET method.

The TGA and DTA measurements were made on a DuPont 951 thermogravimetric analyzer and cell base connected to a Model 990 thermal analyzer. Both measurements were made starting from room temperature up to 1000°C, using a heating rate of 10°C/min. For TGA the samples were heated in nitrogen, while for DTA they were heated in air.

RESULTS AND DISCUSSION

A. Chemical Composition of Catalyst Precursors

The reaction of a metal exchanged Y zeolite with the complex cyanide of a transition metal in solution results in the formation of a water-insoluble complex dispersed throughout the zeolite. The complex is located in the zeolitic cages as well as on the external surface of the zeolite. When reacting Fe^{2+}–Y with $(NH_4)_4[Fe(CN)_6]$, the resulting complex compound contains iron in both cationic and anionic form, as $Fe_2[Fe(CN)_6]$ and $Fe(NH_4)_2[Fe(CN)_6]$. Chemical analysis suggests that some of the iron cations do not react with the complex anions. The negative charges of the zeolitic framework are compensated by ammonium ions initially present in the Fe, NH_4–Y zeolite, by those originated from $(NH_4)_4[Fe(CN)_6]$, as well as by the non-reacted iron cations. Upon oxidation in air

a blue product results, corresponding to "Prussian Blue"—a complex, insoluble compound containing di- and trivalent iron.

By reacting Fe^{2+},NH_4–Y with $K_4[Fe(CN)_6]$, the reactions are similar to those described above, except that potassium ions, the initial ammonium ions, and nonreacted iron cations occupy cationic sites in the zeolite.

The reaction between Co,NH_4–Y zeolite and $(NH_4)_4[Fe(CN)_6]$ results in a mauve product dispersed in the zeolite, consisting primarily of $Co(NH_4)_2[Fe(CN)_6]$, with lesser amounts of $Co_2[Fe(CN)_6]$. Ammonium ions and unreacted cobalt ions occupy cationic sites in the zeolite. A similar composition is likely to be found in the green iron, nickel/zeolite, where the reaction product contains nickel instead of cobalt ions. Similarly, the reaction between Co,NH_4–Y and $K_3[Fe(CN)_6]$ results in $CoK[Fe(CN)_6]$, while some of the cobalt ions remain unreacted in the zeolite.

The reaction between Fe^{2+},NH_4–Y and $K_3[Co(CN)_6]$ yields a pale yellow product. According to Miller and Mathews (16) the reaction between ferrous salts and $K_3[Co(CN)_6]$ results in yellow $Fe_3[Co(CN)_6]_2$. It is reasonable to assume that such a compound is also formed in our reaction. As in previous cases, it appears that only part of the zeolitic ferrous ions react with $K_3[Co(CN)_6]$. The reaction between Cu,NH_4–Y and $Na_2[Fe(CN)_5NO]$ leads to the formation of light-green $Cu[Fe(CN)_5NO]$ in the zeolite. A complex with the same composition and color is obtained by reacting $Na_2[Fe(CN)_5NO]$ with a soluble copper(II) salt. The reaction between Cu,NH_4–Y and $K_3[Co(CN)_6]$ results in the formation of light-blue $CuK[Co(CN)_6]$, similar to the complex obtained with a soluble copper(II) salt. In both zeolitic products, some of the copper ions remain unreacted in the zeolite.

In some instances, the color of the product is different from that of the nonsupported metal complex. This is the case, for instance, with complexes having cobalt in

cationic form. Such differences in color are probably due to different degrees of hydration of the cation, or to different degrees of dispersion.

The fact that only some of the metal cations react with the complex cyanide anion is most likely due to the location of these cations in positions unaccessible to the complex anion (e.g., in the sodalite cage or hexagonal prism). X-Ray data have shown that many transition metal ions occupy, in part, such unaccessible positions in Y zeolites (e.g., *19, 23*). Mössbauer measurements indicate the presence of iron(II) in the sodalite cages of iron-exchanged Y zeolites (*15*).

It is also conceivable that the initially formed reaction products will obstruct some of the zeolite pores, preventing further access of the bulky anions into the zeolite pores. As a result, in most instances the final product contains the anionic metal complex in a lower concentration than theoretically possible. This has to be taken into consideration in the preparation process of catalysts. In the case of a bimetallic catalyst, if one of the two metals has to have a higher concentration, it is this metal that should be in cationic form in the zeolite.

Reduction under hydrogen at 400°C for 4 hr results in all instances in black-gray products. No metal crystallites are detectable by X-ray diffraction. It was found that in the case of iron, reduction of the metal from the cyanide complex occurs more readily than reduction of the same metal in cationic form in the zeolite. The difficulty in reducing the iron in Fe^{2+}–Y has already been mentioned. We have found that calcination of Co^{2+}–Y at 400°C for 8 hr under hydrogen does not result in reduction of the cobalt ions to metallic cobalt. Calcination of the cobalt cyanide complex under hydrogen results in a black-gray product. The nature of this product is not certain, and it is possible that the cobalt remains primarily in some positive oxidation state. Nickel and copper complexes are likely to be reduced

to the metallic form under hydrogen. Further investigation of the reduced products is now in progress. It should be pointed out that the reduced materials act as catalysts, specifically in Fischer–Tropsch reactions.

B. Infrared Spectra

Figure 1 shows the mid-infrared spectra of the catalyst obtained by reacting Fe^{2+}, NH_4–Y with $K_4[Fe(CN)_6]$, before and after reduction in hydrogen. Between 300 and 1300 cm^{-1} both spectra show absorption bands characteristic of the faujasite framework. In addition to these framework vibrations, the band near 1630 cm^{-1} is due to physically retained water and the one at 1400 cm^{-1} to N–H bending vibration. This last band originates in the ammonium ions present in the zeolite. The $[Fe(CN)_6]^{4-}$ complex ion is identified by a fairly strong band near 2080 cm^{-1} (*17*).

The spectrum of the reduced catalyst shows that the band characteristic of the cyanide complex has disappeared. This proves the total destruction of the complex compound during reduction. The band at 1400 cm^{-1} has also disappeared due to the total deammoniation of the zeolite. However, the zeolite framework bands appear unchanged.
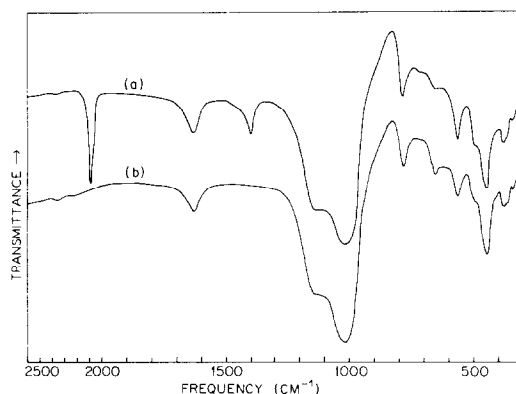

FIG. 1. Infrared spectra for reaction products of Fe^{2+}, NH_4–Y and $K_4[Fe(CN)_6]$; (a) before reduction in H_2; (b) after reduction in H_2 at 400°C for 4 hr.
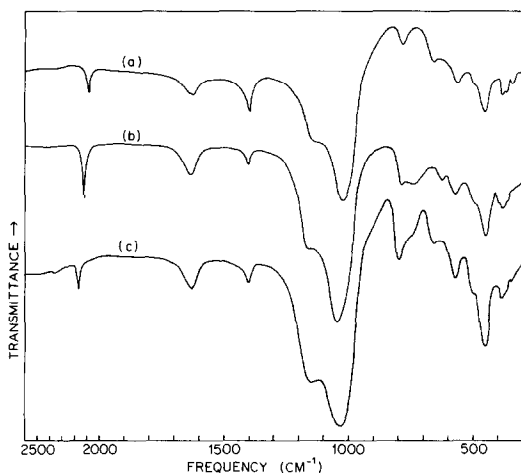
FIG. 2. Infrared spectra of catalysts obtained by reacting (a) Co, NH_4-Y and $(NH_4)_4[Fe(CN)_6]$; (b) Co, NH_4-Y and $K_3[Fe(CN)_6]$; (c) Fe^{2+},NH_4-Y and $K_3[Co(CN)_6]$. Spectra are for nonreduced form.

Figure 2 shows the spectra of three non-reduced catalysts containing iron and cobalt, but prepared by different reactions. Spectra (a), (b), and (c) correspond to the products obtained by reacting Co, NH_4-Y with $(NH_4)_4[Fe(CN)_6]$, Co,NH_4-Y with $K_3[Fe(CN)_6]$, and Fe^{2+},NH_4-Y with $K_3[Co(CN)_6]$, respectively. Spectrum (a) is very similar to one of the nonreduced material in Fig. 1.

The presence of the complex ferrocyanide ion is indicated by the band near 2090 cm^{-1}. The slightly higher frequency of this band as compared to the one in Fig. 1 is probably due to the difference in the nature of cationic species (cobalt vs iron).

Spectrum (b) shows the CN frequency near 2120 cm^{-1} and is characteristic of the $[Fe(CN)_6]^{3-}$ ion. Data in the literature indicate the presence of a CN frequency at 2125 cm^{-1} for $K_3[Fe(CN)_6]$ (17). In spectrum (c) the CN stretching band is located at 2175 cm^{-1} and is due to the $[Co(CN)_6]^{3-}$ ion. The frequency of this band is higher than that corresponding to the CN group in $K_3[Co(CN)_6]$, which is located at 2143 cm^{-1} (17). This shift in frequency is most likely due to the interaction between the cyanocobaltic ion and ferrous ion. It is known (20)

that generally the CN frequency is higher in transition metal salts than in sodium or potassium salts, due to cyano bridging. Moreover, the electrostatic field in the zeolitic cavities is also likely to affect the vibrations in the infrared region.

Figure 3 shows the mid-infrared spectra of several other bimetallic, nonreduced catalysts. Spectra (a), (b), and (c) correspond to catalysts obtained by reacting Cu, NH_4-Y with $K_3[Co(CN)_6]$, Cu,NH_4-Y with $Na_2[Fe(CN)_5NO]$, and Ni,NH_4-Y with $(NH_4)_4[Fe(CN)_6]$, respectively. All three spectra show bands characteristic for the metal cyanide complex: a band at about 2190 cm^{-1} for the compound with $[Co(CN)_6]^{3-}$ ions; bands at 2205 and 1950 cm^{-1} for the compound with $[Fe(CN)_5NO]^{2-}$ ions; and a band at 2095 cm^{-1} for the compound with $[Fe(CN)_6]^{4-}$ ions. In the compound with $[Fe(CN)_5NO]^{2-}$ ions, the band at 2205 cm^{-1} corresponds to the CN frequency, while the one at 1950 cm^{-1} corresponds to the NO stretching frequency (17).

A comparison of spectra obtained for different metal-exchanged zeolites treated with $[Fe(CN)_6]^{4-}$ ions shows a shift of the
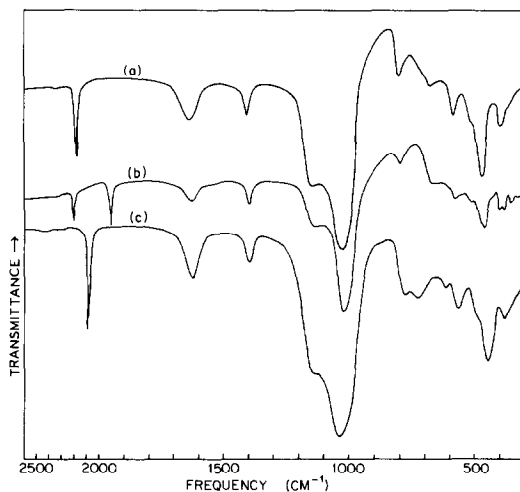

FIG. 3. Infrared spectra of catalysts obtained by reacting (a) Cu, NH_4-Y and $K_3[Co(CN)_6]$; (b) Cu, NH_4-Y and $Na_2[Fe(CN)_5NO]$; (c) Ni, NH_4-Y and $(NH_4)_4[Fe(CN)_6]$. Spectra are for nonreduced form.

CN band to higher frequencies with increasing atomic number in the group Fe, Co, Ni (see corresponding spectra in Figs. 1, 2, and 3). Such a shift can be related to a decrease in ionic radius in the order Fe^{2+}–Co^{2+}–Ni^{2+}, accompanied by a corresponding increase in polarization effect. The increase in CN frequency with decreasing cationic radius has been observed for many metal ferrocyanites (21, 22).

C. DTA and TGA Data

Figure 4 shows the DTA and TGA curves for the material obtained by reacting Fe^{2+}, NH_4–Y and $(NH_4)_4[Fe(CN)_6]$. Chemical analysis suggests that the product contains a mixture of $Fe_2[Fe(CN)_6]$ and Fe, $NH_4[Fe(CN)_6]$ dispersed in the zeolite. Thermal analysis of this material tends to support this interpretation. The broad peak near 200°C is due to loss of ammonia and water. The peaks at 320 and 350°C correspond to the loss of CN. Based on the work done by Mittasch et al. (18) who studied the thermal decomposition of different iron cyanide complexes, it is reasonable to assume that the first peak is due to elimination of NH_4CN, while the second peak is due to the decomposition of the remaining $Fe(CN)_2$.

In Fig. 5 DTA curves for the region up to 550°C are shown for materials obtained by reacting (a) Co,NH_4–Y and $(NH_4)_4$ $[Fe(CN)_6]$; (b) Fe^{2+},NH_4–Y and K_3 $[Co(CN)_6]$; (c) Cu,NH_4–Y and Na_2

FIG. 5. DTA curves for catalysts obtained by reacting (a) Co, NH_4–Y and $(NH_4)_4[Fe(CN)_6]$; (b) Fe^{2+}, NH_4–Y and $K_3[Co(CN)_6]$; (c) Cu,NH_4–Y and $Na_2[Fe(CN)_5NO]$; (d) Co,NH_4–Y and $(NH_4)^3[Fe(CN)_6]$.

$[Fe(CN)_5NO]$. The peaks at 100°C and shoulders near 180°C in curves (a) and (b) are due to the loss of water and ammonia, respectively. In curve (c) only a weak ammonia peak can be detected. Curve (a) shows in the 300–400°C region two peaks characteristic for the two step decomposition of the $[Fe(CN)_6]^{4-}$ ion. However, curve (b) shows that the cyanide loss from the $[Co(CN)_6]^{3-}$ ion occurs in a single step, at 335°C. The material containing $[Fe(CN)_5NO]^{2-}$ ions (curve c) shows a major decomposition at 285°C, while an additional loss occurs at about 300°C. Curve (d) shows that the decomposition of the $[Fe(CN)_6]^{3-}$ ions also occurs in several steps. The decomposition of this ion occurs at a lower temperature than that of $[Fe(CN)_6]^{4-}$, indicating a lower thermal stability.

The thermal decomposition of the metal cyanide complexes depends not only upon the nature of the metals involved, but also upon the environment in which the decomposition takes place. For example, it has been shown (18) that the thermal decompo-
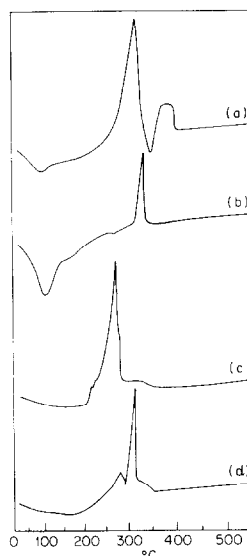

FIG. 4. DTA (a) and TGA (b) curves for catalyst obtained by reacting Fe^{2+},NH_4–Y and $(NH_4)_4[Fe(CN)_6]$.

sition of $Fe_2[Fe(CN)_6]$ under vacuum at 430°C results in a residue of α-Fe, Fe_3C, iron nitride, and carbon. However, in a nitrogen–hydrogen atmosphere, it is easily reduced at 230°C to metallic iron. It is obvious that the later reaction is further enhanced when the reduction is carried out in flowing hydrogen.

ACKNOWLEDGMENTS

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