Thermochimica Acta, 150 (1989) 185–192
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF SUPPORTED $Co_3[Fe(CN)_6]_2$ IN HYDROGEN

QIZE SONG, XIN WANG *, LUDE LU and XUJIE YANG

Modern Chemistry Laboratory, East China Institute of Technology, Nanjing
(People's Republic of China)

(Received 8 February 1989)

ABSTRACT

The thermal decomposition in hydrogen of $Co_3[Fe(CN)_6]_2$ supported on silica, alumina and magnesia was investigated by GC, IR and Mössbauer spectroscopy. As a comparison, the decomposition products of unsupported $Co_3[Fe(CN)_6]_2$ were also measured. Apparently, because of the interaction between the complex and the supports, a portion of the Fe(II) ions was difficult to reduce. On the acidic support, SiO_2, the major gas product was HCN, while on basic supports, the gas products were $(CN)_2$ and N_2.

INTRODUCTION

Supported metal catalysts are usually obtained from supported complexes, which are prepared by ion-exchange or impregnation methods. The properties of supported complexes or their thermal decomposition products have been reported by many authors [1]. But relatively little attention has been paid so far to the details of the decomposition reactions. Bimetal catalysts are widely used in multi-bond hydrogenation [2]. According to the metal energy band theory or the valence bond theory, d electrons play an important role in catalytic activity [3]. In this study, thermal decomposition reactions of $Co_3[Fe(CN)_6]_2$ supported on silica, γ-alumina and magnesia in hydrogen have been investigated. Since CN^- is isoelectronic with N_2 and CO, the study of its hydrogenation reactions would certainly have some bearing on the activated hydrogenation of such small molecules as CO and N_2 [4]. Supported $Co_3[Fe(CN)_6]_2$ has been mentioned as a possible model for bimetal complexes of end-on bonding multi-bond ligands in order to study the effect of the metal on the activation of the multi-bond; the hydrogenation of CN^- was used as a probe during the thermal decomposition.

---

* Author to whom all correspondence should be addressed.

0040-6031/89/$03.50

EXPERIMENTAL

Samples

$Co_3[Fe(CN)_6]_2$, SiO_2, γ-Al_2O_3 and MgO were used as described elsewhere [5,6]. Samples of supported $Co_3[Fe(CN)_6]_2$ were prepared by the reaction of supported $K_3[Fe(CN)_6]$, obtained by impregnation, with $Co(NO_3)_2$ in aqueous solution, washed with water and dried in vacuo. The metal (Co + Fe) content was around 5 wt.% with Co/Fe ratios of 1.55–1.72.

Instrumentation

The gas chromatographic measurements were made as described elsewhere [7]. Infrared spectra were recorded with the Nicolet FT-170SX spectrometer. Mössbauer spectra were measured with an MS-500 Mössbauer spectrometer. The ^{57}Co (Pd matrix) source had an intensity of around 50 mCi. All samples contained from 5 to 15 mg of natural iron/cm^2, were sandwiched between Mylar windows and measured at room temperature. The isomer shifts are reported relative to $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$.

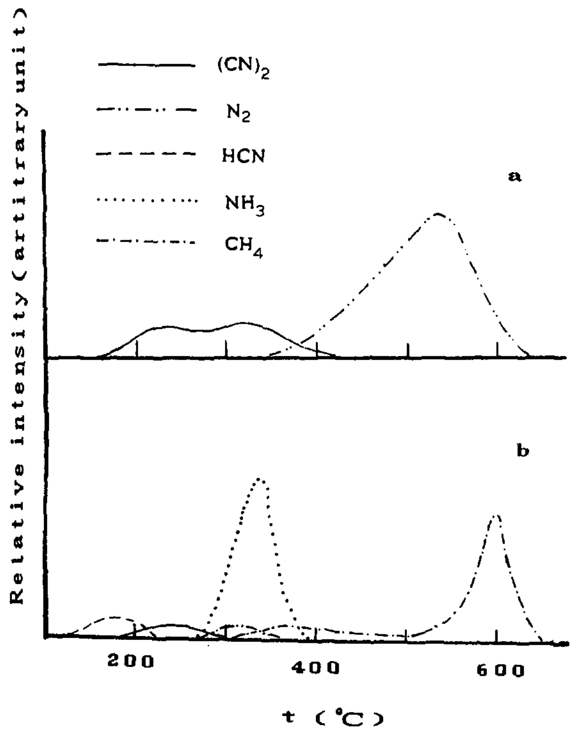

Fig. 1. Thermal decomposition of $Co_3[Fe(CN)_6]_2$ in He (a) and H_2 (b).

RESULTS

When unsupported $Co_3[Fe(CN)_6]_2$ decomposed in He, $(CN)_2$ was released first at 150 °C, and N_2 was expelled above 340 °C (Fig. 1a). In hydrogen, besides $(CN)_2$ and N_2, HCN, NH_3 and CH_4 were produced because of hydrogenation (Fig. 1b). For $Co_3[Fe(CN)_6]_2$–SiO_2, HCN, NH_3, $(CN)_2$ and CH_4 were released as the gas products in hydrogen and no N_2 was detected (Fig. 2a). $Co_3[Fe(CN)_6]_2$–Al_2O_3 gave HCN, $(CN)_2$, NH_3, N_2 and CH_4 (Fig. 2b). No hydrogenation product was found in the thermal decomposition of $Co_3[Fe(CN)_6]_2$–MgO in hydrogen (Fig. 2c).

Both supported and unsupported $Co_3[Fe(CN)_6]_2$ exhibited the CN stretching band at 2130 cm^{-1}. The Fe–C π bond increases the bond order of the Fe–C bond and decreases the bond order of the CN bond. As the lower oxidation state favours the formation of back bonds, the Fe–C bond was more stable and the C–N bond more unstable in $[Fe(CN)_6]^{4-}$ as

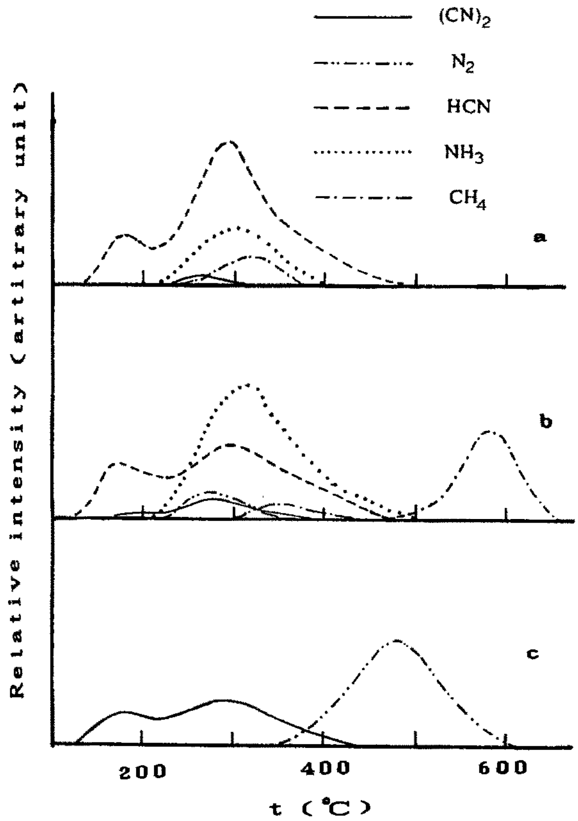

Fig. 2. Thermal decomposition in H_2: a, $Co_3[Fe(CN)_6]_2$–SiO_2; b, $Co_3[Fe(CN)_6]_2$–Al_2O_3; and c, $Co_3[Fe(CN)_6]_2$–MgO.

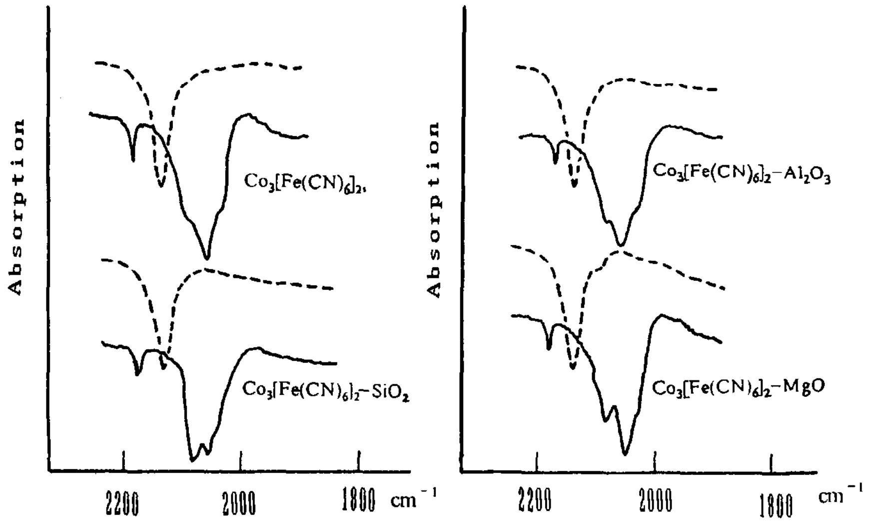

Fig. 3. Infrared spectra: broken line, undecomposed samples; solid line, products at 240 ° C.

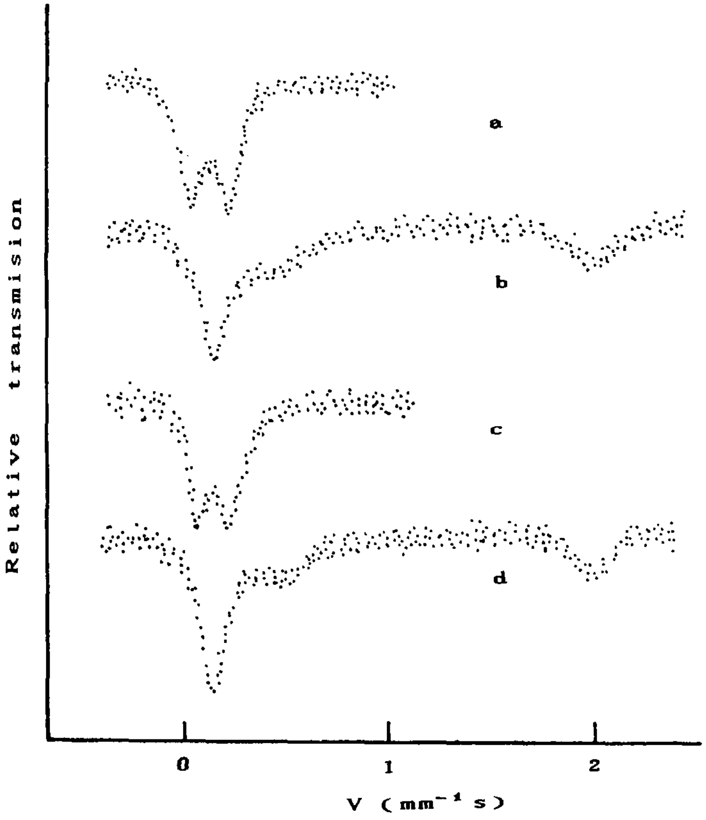

Fig. 4. Mössbauer spectra: a, $Co_3[Fe(CN)_6]_2$; b, its decomposition product at 240 ° C; c, $Co_3[Fe(CN)_6]_2$–SiO_2; and d, its decomposition product at 240 ° C.

TABLE 1

Mössbauer parameters of the samples

Sample	Heating temp. (° C)	Isomer shift δ (mms^{-1})	Quadrupole splitting Δ (mms^{-1})	Internal field (KOe)	Area (%)	Assignment
$Co_3[Fe(CN)_6]_2$	25	0.17	0.15	0	100	low-spin Fe(III)
	240	0.16	0.00	0	65	low-spin Fe(II)
		1.56	1.25	0	35	high-spin Fe(II)
	650	0.30	0.00	344	100	Fe–Co alloy
$Co_3[Fe(CN)_6]_2$–SiO_2	25	0.17	0.18	0	100	low-spin Fe(III)
	240	0.21	0.00	0	68	low-spin Fe(II)
		1.51	1.32	0	32	high-spin Fe(II)
	650	1.23	1.88	0	53	high-spin Fe(II)
		0.31	0.00	343	47	Fe–Co alloy
$Co_3[Fe(CN)_6]_2$–Al_2O_3	25	0.20	0.19	0	100	low-spin Fe(III)
	240	0.20	0.00	0	72	low-spin Fe(II)
		1.52	1.38	0	28	high-spin Fe(II)
	650	1.18	1.77	0	20	high-spin Fe(II)
		0.31	0.00	345	80	Fe–Co alloy
$Co_3[Fe(CN)_6]_2$–MgO	25	0.19	0.19	0	100	low-spin Fe(III)
	240	0.23	0.00	0	64	low-spin Fe(II)
		1.51	1.42	0	36	high-spin Fe(II)
	650	1.10	1.04	0	38	high-spin Fe(II)
		0.32	0.00	345	62	Fe–Co alloy

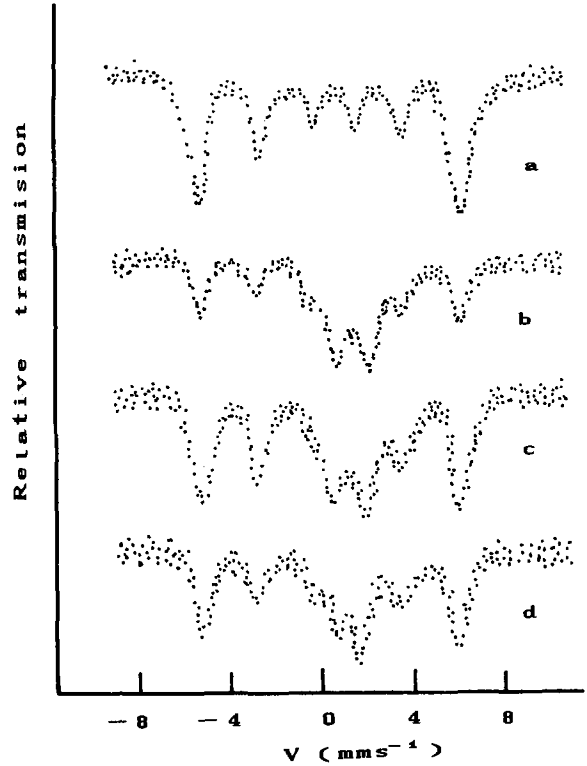

Fig. 5. Mössbauer spectra of decomposition products at 650 °C: a, $Co_3[Fe(CN)_6]_2$; b, $Co_3[Fe(CN)_6]_2$-SiO_2; c, $Co_3[Fe(CN)_6]_2$-Al_2O_3; and d, $Co_3[Fe(CN)_6]_2$-MgO.

compared with those in $[Fe(CN)_6]^{3-}$. Bands at 2074 and 2174 cm^{-1} might be assigned to Fe(II)–CN and Co(II)–CN, respectively (Fig. 3).

In Table 1, it is shown that both the isomer shifts and quadrupole splittings of supported $Co_3[Fe(CN)_6]_2$ were slightly increased relative to the unsupported. This suggests that the small change in the Mössbauer parameters was the result of the effect of the next neighbouring surface groups of the supports. The solid products at 240 °C consisted of two components. The low-spin component might be assigned as $[Fe(CN)_6]^{4-}$, with the Fe(II) ion located in an O_h ligand field and its electronic configuration may be represented as $t_{2g}^6e_g^0$, so that the contribution from the valence electrons and from the ligand field to the electric field gradient was equal to zero, giving a quadrupole splitting of zero. The other Fe(II) ions were in a high-spin state in accordance with the Mössbauer parameters, which implied that they were bound to the CN^- through the nitrogen or located in the holes of the skeleton [8]. In hydrogen at 650 °C, only Fe–Co alloy was obtained from $Co_3[Fe(CN)_6]_2$, while supported complexes produced Fe–Co alloy and highly dispersed Fe(II). Some Mössbauer spectra are shown in Figs. 4 and 5.

DISCUSSION

On the basis of various experimental results, the first stage of the decomposition of supported and unsupported $Co_3[Fe(CN)_6]_2$ was found to be evolution of $(CN)_2$ resulting in the reduction of Fe(III)

$$3Co_3[Fe(CN)_6]_2 \rightarrow 3Co_2[Fe(CN)_6] + Fe_2[Fe(CN)_6] + Co_2[Co(CN)_6] + 3(CN)_2 \qquad (1)$$

Accordingly, as much as 67% Fe(II) in the products was in a low-spin state and this value is close to the results from the Mössbauer spectra (Table 1).

For $Co_3[Fe(CN)_6]_2$, the final product was Fe–Co alloy. According to Johnson et al. [9] and the Mössbauer parameters in Table 1, the Fe/Co ratio of the alloy was approximately 1 : 1. The evolution of N_2 implied that rupture of the C–N bond occurred. As indicated in the IR study for $[Fe(CN)_6]^{4-}$, the Fe–C bond was stronger and the C–N bond weaker as compared with those of $[Fe(CN)_6]^{3-}$, which would favour the production of N_2 and C. The decomposition reactions of the second stage might be considered to proceed according to the following scheme

$$3Co_2[Fe(CN)_6] + Fe_2[Fe(CN)_6] \rightarrow 6FeCo + 12(CN)_2 \qquad (2)$$

$$3Co_2[Fe(CN)_6] + Fe_2[Fe(CN)_6] \rightarrow 6FeCo + 24C + 12N_2 \qquad (3)$$

with reaction (3) predominant.

The final products of supported $Co_3[Fe(CN)_6]_2$ in H_2 contained surface Fe(II) oxide with large quadrupole splittings, indicating that Fe(II) was in a chemical environment of low symmetry and in a highly dispersed state, while FeO with a large particle size would have an NaCl-like lattice with a smaller quadrupole splitting [7]. This suggests that the strong interaction between metal and supports made some of the Fe(II) ions difficult to reduce.

With the exception of $Co_3[Fe(CN)_6]_2$–MgO, in the presence of hydrogen, hydrogenation of $(CN)_2$ takes place [10]

$$(CN)_2 + H_2 \rightarrow 2HCN \qquad (4)$$

and the HCN reacts with H_2 to form NH_3 and CH_4, or C and NH_3

$$HCN + 3H_2 \rightarrow CH_4 + NH_3 \qquad (5)$$

$$HCN + H_2 \rightarrow C + NH_3 \qquad (6)$$

In the range 200–500 ° C, reactions (5) and (6) occurred simultaneously with the latter dominating. On the acidic support, SiO_2, the major gas product was HCN, and on the amphoteric support, Al_2O_3,NH_3 was the major product. On the basic support, MgO, no hydrogenation reaction took place. Therefore, an acid support favours the formation of HCN.

For $Co_3[Fe(CN)_6]_2$ and $Co_3[Fe(CN)_6]_2$–Al_2O_3, the methanation of carbon also took place above 500 ° C.

$$C + 2H_2 \rightarrow CH_4 \qquad (7)$$

In conclusion, it should be emphasized that were it not for the the analysis of both gaseous and solid products in the decomposition of supported $Co_3[Fe(CN)_6]_2$, the complexity of the reaction and the need for an appropriate mechanism would not have been realized.

ACKNOWLEDGEMENT

This investigation was supported by the Fok Ying Tung Education Foundation.

REFERENCES

1 Y.I. Yermakov, B.N. Kuznetsov and V.A. Zakharov, Catalysis by Supported Complexes, Elsevier Sci. Pub. Co., Amsterdam, 1981, pp. 337–405.
2 W.N. Delgass, R.L. Garten and M. Boudart, J. Phys. Chem., 73 (1970) 2970.
3 R.L. Garten, W.N. Delgass and M. Boudart, J. Catal., 18 (1970) 90.
4 W.H. Quayle, G. Peeters, G.L. de Roy, E.F., Vansant and J.H. Lunsford, Inorg. Chem., 21 (1982) 2226.
5 Niu Junning, Wang Xin, Chen Hanwen, Xin Xinquan and Dai Anbang, Chinese Appl. Chem., 6 (1986) 9.
6 Xin Xinquan, Wang Xin, Wu Peicheng and Dai Anbang, J. Mol. Sci., 1 (1985) 123.
7 Wang Xin, Wu Peichen, Xin Xinquan and Dai Anbang, J. Mol. Sci., 3 (1983) 39.
8 A.K. Bonnette and J.F. Allen, Inorg. Chem., 10 (1971) 1613.
9 C.E. Johnson, M.S. Ridont and T.E. Cranshaw, Proc. Phys. Soc., 81 (1963) 1079.
10 Wang Xin, Xin Xinquan, Chen Hanwen and Dai Anbang, Kexue Tongbao, 10 (1985) 613.