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Note

Thermal decomposition of unsupported and supported $Sn_3[Fe(CN)_6]_4$ in air

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Abstract

The thermal decomposition of unsupported and supported $Sn_3[Fe(CN)_6]_4$ in air has been studied by IR and Mössbauer spectroscopies. The first stage of decomposition of $Sn_3[Fe(CN)_6]_4$ was found to be evolution of $(CN)_2$ resulting in the reduction of Fe(III); for the supported $Sn_3[Fe(CN)_6]_4$, most of the Fe(III) became high-spin as a result of the effect of the supports. Above 400 °C, the final products of $Sn_3[Fe(CN)_6]_4$ gave a Mössbauer spectrum which consisted of a super-paramagnetic doublet and a hexad; with the exception of $Sn_3[Fe(CN)_6]_4$-AC, the final products of the supported compound contained two kinds of Fe(III) oxide with different quadrupole splittings.

INTRODUCTION

Supported complexes have been extensively studied in the last few years due to their extended use in catalytic processes [1]. The activity and selectivity of the catalysts can be improved considerably by using alloys instead of pure metals; the discovery of bimetallic catalysts is one of the important developments in heterogeneous catalysis [2,3]. A fundamental problem of catalysis by supported metals is to clarify the cause of formation of the catalysts. In recent years this domain of catalysis has occupied special attention. The studies of thermal decompositions of supported complexes may offer new approaches to this problem. Baibich et al. [4] used IR and Mössbauer spectroscopies to study the interaction of $Fe_3(CO)_{12}$ and a mixture of $Fe_3(CO)_{12}$/Ni(acac)$_2$ with alumina, and the products of their thermal decomposition in different conditions. Reactions of $Co_3[Fe(CN)_6]_2$, H_2PtCl_6 and $Co(HCOO)_2$ on supports have been reported [5-7].

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We report herein the thermal decomposition of supported $Sn_3[Fe(CN)_6]$ in air using IR and Mössbauer spectroscopies which have been shown to be very efficient in the identification of the chemical state of the decomposition products.

EXPERIMENTAL

Samples

$Sn_3[Fe(CN)_6]_4$ was prepared by the deposition method using $SnCl_4$ and $K_3[Fe(CN)_6]$ aqueous solutions, followed by washing with water, filtering, and drying in vacuo at 100 °C for 48 h. Silica, γ-alumina, magnesia and activated carbon (AC) were used as described elsewhere [8,9]. Samples of supported $Sn_3[Fe(CN)_6]_4$ were prepared by the reaction of supported $K_3[Fe(CN)_6]$, obtained by impregnation, with $SnCl_4$ in aqueous solution, washed with water and dried in vacuo at 80 °C for 48 h. The metal (Sn + Fe) was around 4 wt.% with Sn/Fe atomic ratios of 0.72–0.76.

Instrumentation

Infrared spectra were recorded with the Nicolet FT-170SX spectrometer using the KBr pellet technique. Mössbauer spectra were measured with an

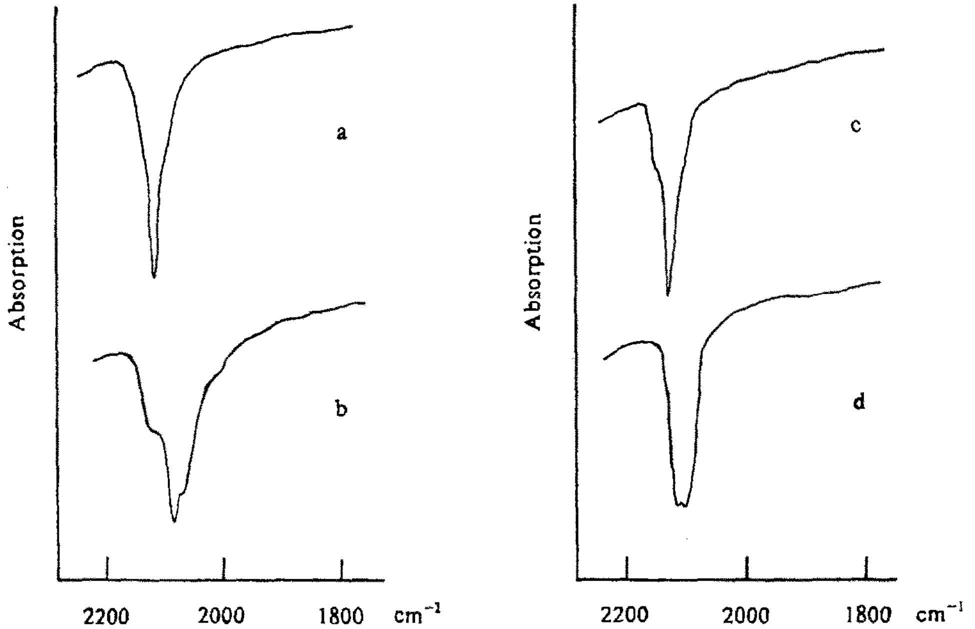

Fig. 1. Infrared spectra in the range of 2200–1800 cm^{-1}. Curve a, $Sn_3[Fe(CN)_6]_4$; curve b, $Sn_3[Fe(CN)_6]_4$ at 260 °C; curve c, $Sn_3[Fe(CN)_6]_4$–Al_2O_3; and curve d, $Sn_3[Fe(CN)_6]_4$-Al_2O_3 at 260 °C.

Elscint Mössbauer spectrometer. The ^{57}Co (Rh-matrix) source had an intensity of around 10 mCi. The isomer shifts are reported relative to $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$. The ^{119}Sn Mössbauer spectra were also recorded. The decomposition apparatus was used as described elsewhere [8].

RESULTS AND DISCUSSION

Typical IR and Mössbauer spectra of the samples are shown in Figs. 1 and 2. The ^{57}Fe Mössbauer parameters are listed in Table 1. It should be pointed out that the change in the Mössbauer parameters of undecomposed supported $Sn_3[Fe(CN)_6]_4$, as compared with that of the unsupported compound, was not noticeable, and only Sn(IV) was found for all samples in the ^{119}Sn Mössbauer spectra; therefore, these data are not listed.

Both supported and unsupported $Sn_3[Fe(CN)_6]_4$ exhibited the CN stretching band at around 2115 cm^{-1}. The strong band of the products at

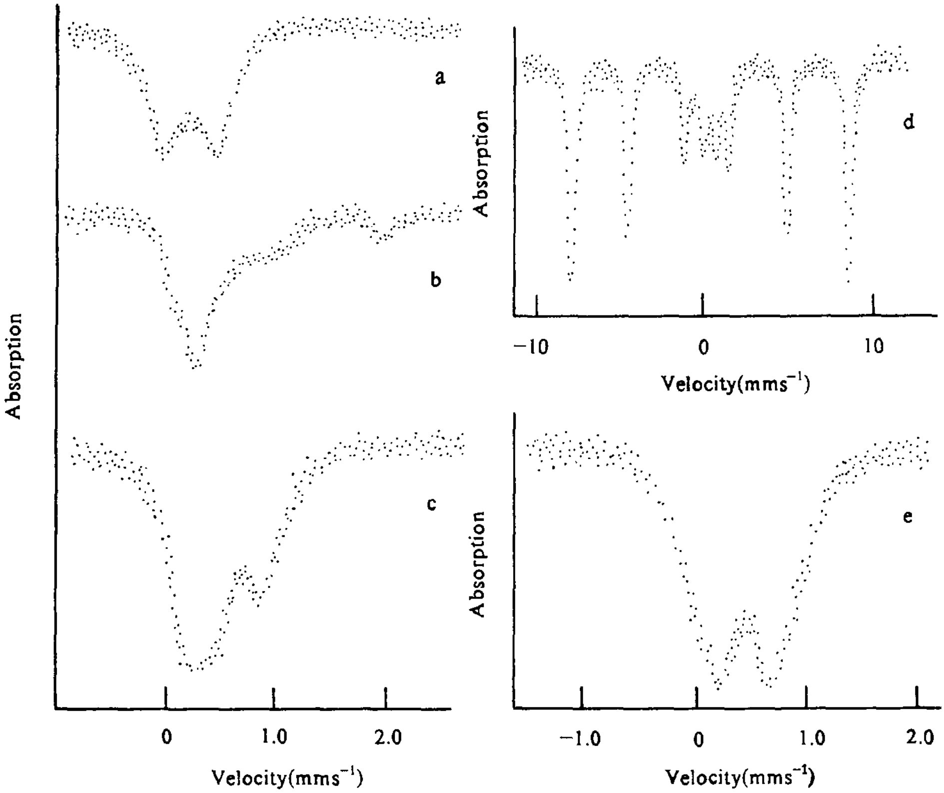

Fig. 2. Mössbauer spectra. Curve a, $Sn_3[Fe(CN)_6]_4$; curve b, $Sn_3[Fe(CN)_6]_4$ at 260 °C; curve c, $Sn_3[Fe(CN)_6]_4$–Al_2O_3 at 260 °C; curve d, $Sn_3[Fe(CN)_6]_4$ at 400 °C; and curve e, $Sn_3[Fe(CN)_6]$–Al_2O_3 at 400 °C.

TABLE 1

Mössbauer parameters of unsupported and supported $Sn_3[Fe(CN)_6]_4$

Support	Heating temp. (°C)	Isomer shift δ (mm s^{-1})	Quadrupole splitting Δ (mm s^{-1})	Area (%)	Assignment
	25	0.160	0.480	100	low-spin Fe(III)
	260	0.162	0.523	18	low-spin Fe(III)
		0.210	0.000	67	low-spin Fe(II)
		1.220	1.341	15	high-spin Fe(II)
	400	0.620	0.743	13	high-spin Fe(III)
		0.661	0.000	87	high-spin Fe(III) [a]
MgO	260	0.212	0.000	46	low-spin Fe(II)
		0.619	0.401	54	high-spin Fe(III)
	400	0.604	0.410	75	high-spin Fe(III)
		0.508	0.897	25	high-spin Fe(III)
Al_2O_3	260	0.206	0.000	40	low-spin Fe(II)
		0.652	0.475	60	high-spin Fe(III)
	400	0.604	0.476	68	high-spin Fe(III)
		0.600	1.013	32	high-spin Fe(III)
SiO_2	260	0.201	0.000	35	low-spin Fe(II)
		0.648	0.427	65	high-spin Fe(III)
	400	0.608	0.431	48	high-spin Fe(III)
		0.615	0.859	52	high-spin Fe(III)
AC	260	0.196	0.000	26	low-spin Fe(II)
		1.602	1.372	6	high-spin Fe(III)
		0.633	0.532	68	high-spin Fe(III)
	400	0.653	0.692	44	high-spin Fe(III)
		0.662	0.000	56	high-spin Fe(III) [b]

[a] Internal field = 512 KOe.

[b] Internal field = 511 KOe.

260 °C at around 2080 cm^{-1} may be assigned to Fe(II)–CN. In addition to a small amount of undecomposed $Sn_3[Fe(CN)_6]_4$, the solid products of $Sn_3[Fe(CN)_6]_4$ at 260 °C consisted of two Fe(II) components, which have been assigned to high-spin Fe(II) and low-spin Fe(II), respectively (Table 1). On the basis of these experimental results, the first stage of the decomposition of $Sn_3[Fe(CN)_6]_4$ was found to be evolution of $(CN)_2$ resulting in the reduction of Fe(III)

$$3Sn_3[Fe(CN)_6]_4 \rightarrow Fe_2[Fe(CN)_6] + 9Sn[Fe(CN)_6] + 6(CN)_2 \tag{1}$$

Theoretically, it is expected that the low-spin Fe(II)/high-spin Fe(II) ratio will be 5.0; this value is close to the area ratio of Mössbauer spectra of 4.5 (67/15). However, for supported $Sn_3[Fe(CN)_6]_4$ at 260 °C, most Fe(III) became high-spin, indicating that oxygen replaced the CN^- ligands.

The products of $Sn_3[Fe(CN)_6]$ resulting from burning in air above 400 °C consisted of two Fe(III) oxides, one with a super-paramagnetic doublet, indicating that the particles were very small, while as much as 87% Fe_2O_3 had a six-fold spectrum due to the larger particle size.

With the exception of $Sn_3[Fe(CN)_6]_4$-AC, the final products of supported $Sn_3[Fe(CN)_6]_4$ contained two kinds of Fe(III) oxides with different quadrupole splittings, indicating that a portion of the Fe(III) with larger quadrupole splittings were in a chemical environment of low symmetry and in a highly dispersed state as a result of the strong interaction between metal and supports, while, relatively, the remainder had a larger particle size. The decomposition of $Sn_3[Fe(CN)_6]$-AC was somewhat similar to that of the unsupported compound.

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