

STUDIES ON SOLID STATE REDOX REACTION OF IRON(III) OXALATE BY GAS CHROMATOGRAPHY

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ABSTRACT

The solid state redox reaction of iron (III) oxalate with sodium nitrate and tin(II) chloride was investigated in hydrogen atmosphere and helium atmosphere by use of a non-isothermal technique. The evolved gases (EG) formed during the reaction were directly detected by gas chromatography, and the solid products were also identified by XRD, Mössbauer spectra and IR. The results show that the solid state redox reaction can go to completion because electron transfer is much easier than mass diffusion along the boundaries of the reactant. The releasing of crystal and coordination water during the redox reaction also facilitates completion of the reaction. The mechanism of the solid state reaction is also discussed.

INTRODUCTION

Solid state reaction is widely used in ceramics, metallurgy, special material making and catalyst manufacture [1,2]. The characteristic of the solid state reaction is that the reactants are in solid state and most of the reaction products are also in solid state. The reaction normally takes place at higher temperature in heterogeneous phase. The control and detection of the reaction are more difficult than in the liquid or gaseous phase. Solid state reaction needs more intensive research to throw some light on this obscure field [3].

In the past decade the routine methods for the accurate and rapid determination of temperature or energy changes associated with solid state reaction have been the thermal analytical methods such as DTA, DSC and DC. In DSC, the same is subjected to a known heating program, either in scanning mode or under isothermal conditions, and the energy changes arising from thermal events inside the sample are monitored as a function of the temperature of an inert reference which is simultaneously subjected to the same heating program. It is obvious that these techniques cannot provide

information about the products produced during solid state reaction and are little help in clarifying the chemical reaction mechanism.

In our laboratory an on-line gas chromatography apparatus was constructed which provides a powerful technique to detect all of the gaseous products evolved during the reaction and to monitor the reaction, because of its high separation and quantitative determination ability. The data obtained by on-line gas chromatography are very helpful in revealing the mechanism of the reaction, and the different reactions at different stages. In this paper the solid state redox reaction of iron(III) oxalate with inorganic salts are investigated mainly by gas chromatography accompanied by Mössbauer spectra, IR and XRD. The solid and gaseous products are identified and the reaction mechanism is also discussed.

EXPERIMENTAL

Reactants of analytical grade were used throughout in this research. A Suchua model SC-6 gas chromatograph was used; 0.3×300 cm stainless steel column, column chamber temperature 120°C , TCD 150°C , vaporization chamber 140°C , bridge current 150 mA, carrier gas flow rate 60 ml min^{-1} , Porapark QS 80–100 mesh is used as column material. For the separation of O_2 and NO from CO the same length column packed with 13 X molecular sieve is used as the separation column and the column chamber temperature lowered to 25°C . A six-way stop cock for sample entrance is heated by an external electrical heating belt to about 100°C to prevent condensation of water vapor. Retention time, peak area and peak height are printed out by Hewlett 3390A integrator.

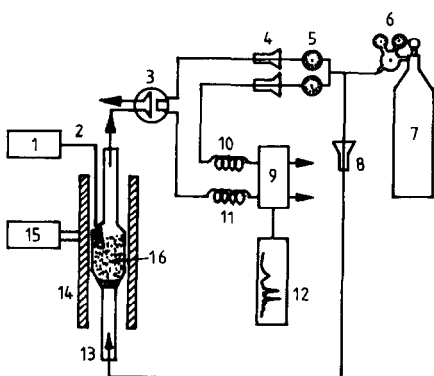


Fig. 1. Schematic diagram of the solid state reaction apparatus. 1, Thermocouple temperature recorder; 2, chromel–alumel thermocouple; 3, six-way stop cock; 4, flow rate regulator; 5, barometer; 6, pressure relief valve; 7, cylinder; 8, flow rate regulator for reaction gas; 9, TCD; 10, reference column; 11, separation column; 12, gas chromatogram recorder; 13, reaction Pyrex tube; 14, furnace; 15, furnace temperature controller; 16, sample.

The heating rate of the electrical furnace is controlled by a linear heating programmer; the typical heating rate is $5^{\circ}\text{C min}^{-1}$. There is a 2 cm isothermal field in the middle of the furnace and the sample is placed in this area. The sample tube is made of Pyrex or quartz and a tube window is provided for temperature measurement by a chromel–alumel thermocouple. The gaseous products formed during the reaction are carried into the six-way stopcock by reaction gas at a flow rate of 40 ml min^{-1} . The reaction gas is helium or hydrogen according to the atmosphere of the reaction.

The powder X-ray diffraction patterns of the solid state redox reaction products is recorded by a Shimadzu model XD-3A X-ray diffractometer with a copper target; high voltage 25 kV, current 20 mA, slit width 0.3 mm. The IR spectra are recorded by a Nicolet-FT-IR-107-Sx IR spectrometer using the KBr pellet method.

Mössbauer spectra are measured in an AH-803 Mössbauer spectrometer and the source of radiation is $^{57}\text{Co/Rh}$, strength 20 mCi. The iron absorbent contains 5–10 mg iron. The sample is heated to a certain temperature in hydrogen or in helium atmosphere, then cooled and transferred and covered with a layer of wax to prevent the air oxidation of sample during measurement; the Mössbauer parameter is calculated from the experimental data by PC/XT microcomputer using Larentz curve simulation. Alpha-Fe is used as the standard.

RESULTS AND DISCUSSION

The solid state redox reaction of iron oxalate and sodium nitrate

Figure 2a shows the distribution of evolved gaseous products of iron oxalate during thermal decomposition in hydrogen atmosphere (EG curve), which is determined by on-line gas chromatography. There are two peaks in Fig. 2a, the first one at 180°C shows the releasing of CO_2 and H_2O during auto-reduction of iron(III) oxalate into $\alpha\text{-FeC}_2\text{O}_4$; the other at 350°C shows the evolution of the gaseous products CO and CO_2 , coming from the thermal decomposition of $\alpha\text{-FeC}_2\text{O}_4$. The lagged CH_4 peak means the catalytic effect of iron for methanation, and the water peak results from the reduction of FeO into $\alpha\text{-Fe}$ by hydrogen as proved by Mössbauer spectra [4].

Figure 2b is the EG curve of the evolved gaseous products during the thermal decomposition of sodium nitrate in hydrogen atmosphere, and it can be seen that sodium nitrate is stable up to 500°C in hydrogen atmosphere, which is consistent with results reported in the literature [5].

Figures 2c and 2d are the EG curves of the solid state redox reaction between iron oxalate and sodium nitrate in hydrogen and helium atmo-

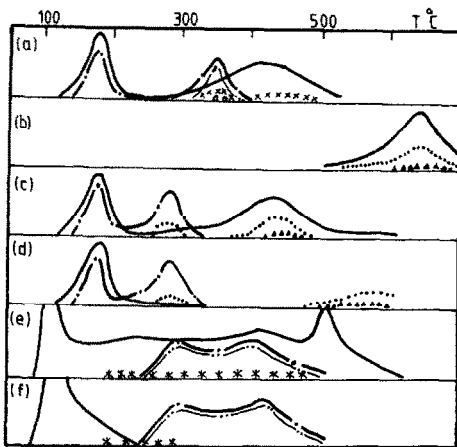


Fig. 2. EG curves of solid state redox reaction of iron oxalate with sodium nitrate and tin chloride. a, Iron(III) oxalate in hydrogen; b, sodium nitrate in hydrogen; c, 1:5 mole iron oxalate and sodium nitrate in hydrogen; d, 1:5 mole iron oxalate and sodium nitrate in helium; e, 1:3 mole iron oxalate with tin chloride in hydrogen; f, 1:3 mole iron oxalate with tin chloride in helium. — H_2O ; O_2 , NO; ▲▲▲ NO_2 ; - - - CO_2 ; ●—● CO; ××× CH_4 ; *** HCl; ○○○ C_2 .

sphere respectively. The sample size is in the 80–100 mesh range, and during the experiment the samples are kept out of direct sunlight to prevent iron oxalate from light induced decomposition. There are three peaks in Figs. 2c and 2d, the first one located at 180°C , in both H_2 atmosphere and He atmosphere. The shape is the same as the first peak in Fig. 2a, implying that the same reaction occurred around 180°C . The second one falls in the range $260\text{--}300^\circ\text{C}$, lower than the second peak in Fig. 2a. Large amounts of CO_2 and a little O_2 , NO and H_2O are released at this stage, but there is no CO evolved which excludes the possibility of the thermal decomposition of $\alpha\text{-FeC}_2\text{O}_4$ which should give off CO and CO_2 simultaneously. Thus it can be inferred that the solid state reaction occurred at this stage. This inference is supported by Mössbauer spectra and XRD. The third peak appeared around 440°C in hydrogen atmosphere which shows the releasing of NO, O_2 , NO_2 and H_2O but no CO and CO_2 evolution must result from the decomposition of nitrate salts.

Figure 3 shows the Mössbauer spectra at room temperature of the reaction products of iron oxalate with sodium nitrate reacted at different temperatures. Table 1 lists the Mössbauer parameters calculated from the spectra, and the assignments are also given. From these spectra it can be seen that at 60°C iron was in high spin state Fe(III); at 260°C most of it changed to high spin state Fe(II) as a result of the self-reduction process of iron(III) oxalate at 180°C [4], and at 360°C all of the iron was in high spin state Fe(III), which must have been the result of the redox reaction of $\alpha\text{-FeC}_2\text{O}_4$ with sodium nitrate at $260\text{--}300^\circ\text{C}$. In the light of Figs. 2c

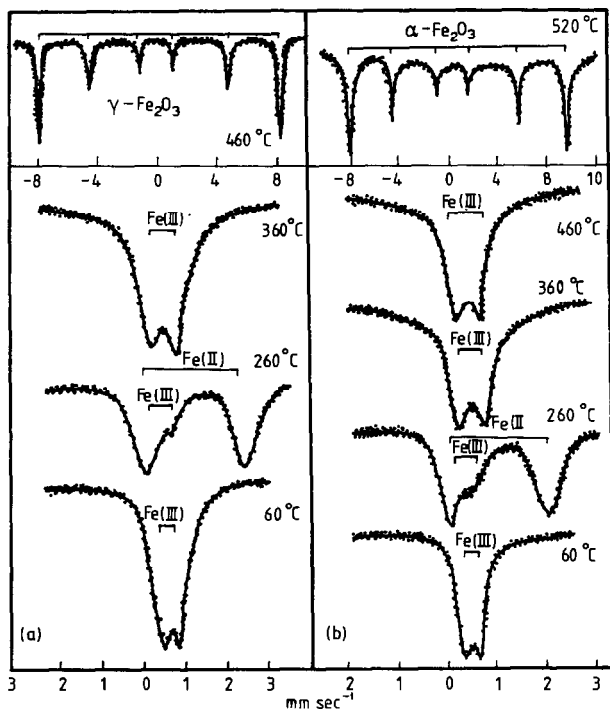


Fig. 3. Mössbauer spectra of the solid products of iron(III) oxalate with sodium nitrate at various temperatures (a) in hydrogen atmosphere; (b) in helium atmosphere.

TABLE 1

Room temperature Mössbauer parameters of solid reaction products of iron(III) oxalate with sodium nitrate at various temperatures in hydrogen and helium atmosphere

Atmos.	Temp. (°C)	δ (mm sec ⁻¹)	ΔE_Q (mm sec ⁻¹)	Γ (mm sec ⁻¹)	H_i (kOe)	Area (%)	Assignment
H ₂	60	0.61	0.36	0.38		100	Fe ₂ (C ₂ O ₄) ₃
	260	0.77	0.54	0.43		10	Fe(III)
		1.46	2.26	0.55		90	α -FeC ₂ O ₄
	360	0.59	0.65	0.63		100	Fe(III)
	460	0.22	0.05	0.11	491	100	γ -Fe ₂ O ₃
He	60	0.61	0.36	0.38		100	Fe ₂ (C ₂ O ₄) ₃
	260	0.72	0.65	0.44		20	Fe(III)
		1.42	2.29	0.42		80	α -FeC ₂ O ₄
	360	0.69	0.59	0.52		100	Fe(III)
	460	0.59	0.72	0.54		100	Fe(III)
	520	0.38	0.35	0.20	523	100	α -Fe ₂ O ₃

δ , Chemical shift; ΔE_Q , quadrupolar splitting; Γ , peak width at half height; H_i , internal magnetic field.

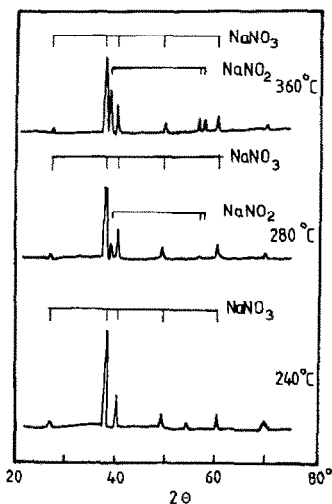


Fig. 4. XRD results of the solid products of iron(III) oxalate with sodium nitrate at different temperatures in hydrogen atmosphere.

and 2d, it can be concluded that difference of atmosphere has no effect on the solid state redox reaction. At 460 °C γ - Fe_2O_3 was formed in hydrogen atmosphere while NaNO_3 and NaNO_2 decomposed, whereas in helium atmosphere no Fe_2O_3 was formed in this stage because NaNO_3 and NaNO_2 are stable below 500 °C. At 520 °C in helium NaNO_3 and NaNO_2 began decomposing and Fe(III) was transformed into α - Fe_2O_3 .

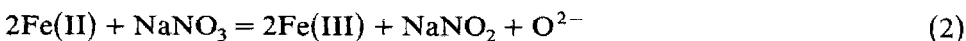
Figure 4 shows the XRD results. It can be observed that no NaNO_2 was formed before 240 °C; at 280 °C NaNO_2 began presenting, and at 360 °C the relative height of the diffraction peak of NaNO_2 was increased, indicating that NaNO_2 was one of the solid state reaction products.

From the above discussion, the following conclusions may be drawn: at 180 °C auto-reduction reaction takes place



The gaseous products CO_2 and H_2O were detected by gas chromatography (Figs. 2c and 2d) and the solid product α - FeC_2O_4 was proved by Mössbauer spectra.

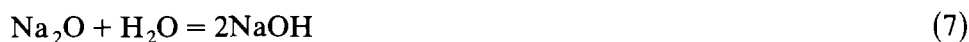
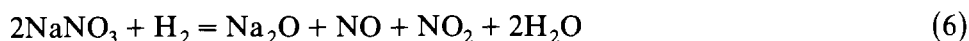
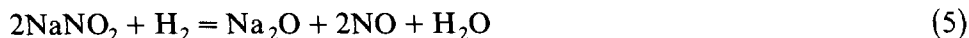
From 260 to 300 °C redox reactions take place



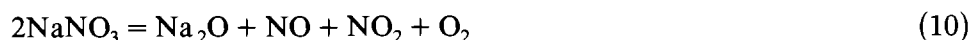
The gaseous products are detected by EG (Figs. 2c and 2d), sodium nitrite and the spin state of iron are determined by XRD and Mössbauer spectra (Figs. 3 and 4), respectively. Because the main step of the redox reaction

involves the electron transfer which is much easier than mass diffusion along the boundaries of the reactants, the redox reaction is complete so that there is no CO and CO₂ evolved after the redox reaction.

Above 380 °C in hydrogen atmosphere, sodium nitrite and sodium nitrate gradually decomposed; O₂, NO and NO₂ are released. As a result of the reducing reaction of hydrogen, water also emerged; meanwhile Fe(III) transformed to gamma-Fe₂O₃



In the helium atmosphere, water emerged above 250 °C; the last peak on the EG curve (Fig. 2e) lagged behind compared with that in the hydrogen atmosphere, which lowered the decomposition temperature of NaNO₂ and NaNO₃. The decomposition reactions in helium are as follows



The formation of alpha-Fe₂O₃ is shown by Mössbauer spectra.

Redox reaction of iron(III) oxalate and tin(II) chloride

The EG curves of 80–100 mesh solid mixtures of iron oxalate and tin(II) chloride in 1 : 3 mole ratio in hydrogen atmosphere and helium atmosphere are shown in Figs. 2e and 2f respectively. Compared with Fig. 2a, the difference is obvious, and the redox reaction may be divided into three stages. In the first stage from 80 to 200 °C, a lot of water was released but no CO₂ was evolved, indicating no iron(III) oxalate in the system, otherwise CO₂ should be released at 180 °C. The second stage occurred at 210–350 °C, when nearly equal amounts of CO and CO₂ were released, which must have been resulted from the cleavage of oxalate anion. When the temperature was higher than 200 °C, HCl gas was evolved. The third stage took place at 350–490 °C with more CO and CO₂ released from the further cleavage of oxalate anion, and in hydrogen atmosphere water was also formed by the gas–solid reaction.

Figure 5 shows the IR spectra of the solid state reaction products in hydrogen atmosphere. It shows that the characteristic vibration bands of C₂O₄²⁻ appeared at 25, 250 and 340 °C but disappeared at 500 °C.

Figure 6 shows the XRD results of the solid state redox reaction products of iron(III) oxalate with tin(II) chloride in hydrogen atmosphere. The

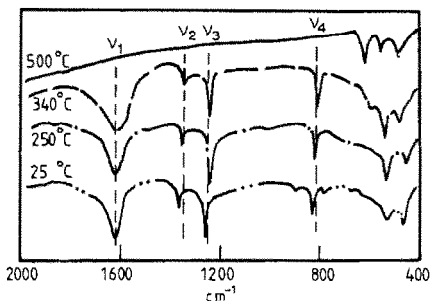


Fig. 5. IR spectra of the solid redox reaction products of iron(III) oxalate with tin(II) chloride in hydrogen atmosphere. ν_1 : $\nu_{as}(\text{C}=\text{O})$, ν_2 : $\nu_s(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$, ν_3 : $\nu_s(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$, ν_4 : $\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$ [6].

diffraction peaks are identified and marked. It can also be observed that the main decomposition products at 25 °C were the same as those at 200 °C and that FeSn alloy was formed at 550 °C.

Figure 7 shows the Mössbauer spectra of the solid state reaction products of iron(III) oxalate and tin(II) chloride in hydrogen atmosphere and Table 2 lists the Mössbauer parameters. It can be seen that between 25 and 340 °C, iron was high spin state Fe(II), consistent with $\alpha\text{-FeC}_2\text{O}_4$, and that at 550 °C a sextet spectrum was recorded which provides further evidence of the formation of FeSn alloy.

From the above experimental results, the mechanism of the solid state redox reaction between iron(III) oxalate and tin(II) chloride may be postulated. At room temperature, the following solid state redox reaction takes place

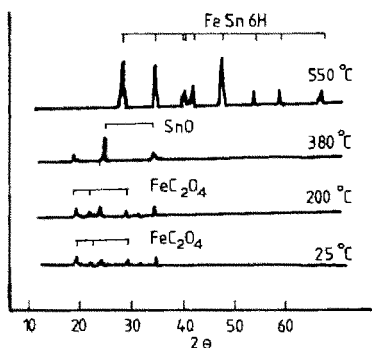
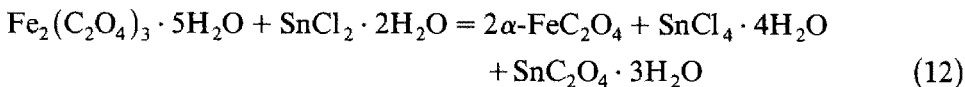


Fig. 6. XRD results of the solid state redox reaction products of iron(III) oxalate with tin(II) chloride in hydrogen atmosphere.

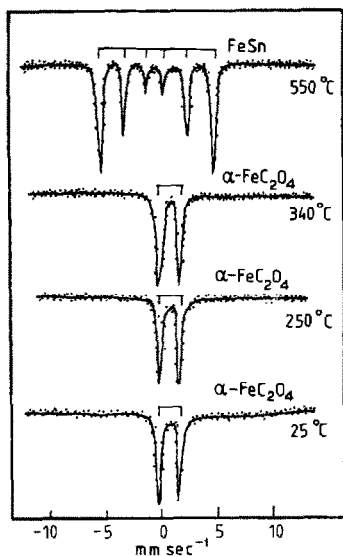


Fig. 7. Mössbauer spectra of the solid state redox reaction products of iron(III) oxalate with tin(II) chloride in hydrogen atmosphere.

At 80–200 °C water evolved, and this is shown by the EG curve (see Fig. 2). When the temperature rose further (> 200 °C), a part of the SnCl_4 hydrolyzed releasing HCl, and a part was reduced by hydrogen producing HCl; meanwhile SnC_2O_4 decomposed to SnO with evolution of CO and CO_2



At 400 °C FeC_2O_4 began decomposing into FeO, CO and CO_2 ; FeO was then reduced by hydrogen to $\alpha\text{-Fe}$ and SnO, SnCl_2 were also reduced with

TABLE 2

Room temperature Mössbauer parameters of solid reaction products of iron(III) oxalate with tin(II) chloride at various temperatures in hydrogen atmosphere

Temp. (°C)	δ (mm sec ⁻¹)	ΔE_Q (mm sec ⁻¹)	Γ (mm sec ⁻¹)	H_1 (kOe)	Area (%)	Assignment
25	1.16	1.73	0.14		100	$\alpha\text{-FeC}_2\text{O}_4$
250	1.16	1.78	0.14		100	$\alpha\text{-FeC}_2\text{O}_4$
340	1.10	1.80	0.16		100	$\alpha\text{-FeC}_2\text{O}_4$
550	0.05	0.00	0.16	331	100	FeSn

δ , Chemical shift; ΔE_Q , quadrupolar splitting; Γ , peak width at half height; H_1 , internal magnetic field.

the formation of FeSn alloy. The thermal decomposition of α -FeC₂O₄ was delayed on account of the presence of metal chloride, as indicated by IR and XRD [7].

The solid state redox reaction of iron oxalate with tin chloride in helium was almost the same as that in hydrogen atmosphere. A part of the SnCl₄ was also hydrolyzed, releasing HCl, but there was no reduction of SnCl₄ in helium. The decomposition of α -FeC₂O₄ was also delayed owing to the presence of tin chloride [7].

From the above discussion, it is obvious that the solid state redox reaction can be completed at relatively low temperature because the electron transfer is much easier than the mass diffusion along the boundaries of the reactants and the release of water during the reaction also enhances the process of the solid state redox reaction. Results of the present study serve to show that the application of gas chromatography to solid state reaction investigation has many advantages over the classical methods of DSC, DTA and TG, and that EG curves of the reaction reflect the various steps of the solid state reaction so long as there is gas formed and evolved.

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