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Thermal degradations of some layer-type complexes consisting of FeOCl and organic compounds

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FeOCl crystals were intercalated with furfural, furfuryl alcohol and 2-vinyl pyridine. The resulting layer-type complexes, with or without γ-radiation, were thermally degradated. Thermal stabilities of all complexes were lower than that of FeOCl. FeOCl maintained its layered structure up to 773 K but FeOCl–furfural complex, which is the most stable, began to degrade at 423 K. Through the degradations, FeOCl changed into Fe_2O_3 and Fe_3O_4, and FeOCl–furfural complex into Fe_3O_4, $FeCl_2$ and an unidentified compound. The causes of such differences are discussed.

1. Introduction

Previously, we reported on the behaviour of thermal degradation of the layer-type complex consisting of montmollironite and α-naphthylamine [1]. The layered structure of montmollironite decomposed into β-quartz and μ-cordierite at about 1073 K but the layer-type complex maintained its layered structure up to 1273 K. We thought, therefore, that these phenomena suggest: (i) thermal stability of a layered structure of an inorganic compound is enhanced by intercalating with an organic compound; (ii) a new or unique compound forms by decomposing such a complex of inorganic and organic compounds, and (iii) a layer-type complex of an inorganic compound and carbon is prepared. These possibilities may lead to the development of new materials with attractive properties. From these standpoints, we decided to investigate the thermal degradation behaviour of a series of layer-type complexes of inorganic and organic compounds.

FeOCl is known to have a layered structure and to intercalate with some inorganic compounds to result in layer-type complexes [2]. In the present work, therefore, the layer-type complexes of FeOCl and some organic compounds were prepared and subsequently heat-treated to various temperatures to study the possibilities stated above.

2. Experimental details

2.1. Materials

FeOCl crystals (0.246 to 0.991 mm) were prepared according to the procedures given by Kanamaru *et al.* [2] and were intercalated with furfural ($C_5H_4O_2$), furfuryl alcohol ($C_5H_6O_2$) and 2-vinyl pyridine (C_7H_7N), respectively. These organic compounds polymerize so readily when allowed to stand at room temperature that they were distilled immediately before use.

2.2. Preparation and heat-treatment of the resultant complexes

FeOCl and an acetone solution of an organic compound were sealed in the pyrex glass tubing under vacuum, followed by retention under conditions indicated in Table I. After retention, organic compounds attached to the crystal surfaces were washed away with acetone and were then used for X-ray diffraction and element analyses.

The layer-type complexes thus prepared were sealed again in the pyrex glass tubing under vacuum, followed by γ-radiation using Co-60 (12 Mrad) to polymerize the inserted organic compounds. The complexes were subsequently heated to various temperatures below 773 K at a heating rate of $3\,\mathrm{K\,min^{-1}}$ and held for 0.5 h. These complexes were also heated under nitrogen. For the references, FeOCl and complexes without

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TABLE I Preparation conditions of the complexes consisting of FeOCl and organic compounds

Abbreviations	FeOCl (g)	Solution (ml)		Residence	
		Organic compound	Acetone	Temperature (K)	Time (day)
IFC	0.5	5 (furfural)	5	323	10
IVC	0.5	2 (2-vinyl pyridine)	8	353	8
IAC	0.5	2.5 (furfuryl alcohol)	7.5	303	2

γ-radiation were heated under the same conditions used for the γ-radiated complexes. The resulting degradation products were identified using X-ray diffraction techniques.

3. Results

3.1. Structures of the complexes

As shown in Table I, the complexes of FeOCl and furfural, 2-vinyl pyridine and furfuryl alcohol are abbreviated as IFC, IVC and IAC in the text. Table I suggests big differences in ease of the complex formations of organic compound and FeOCl.

The basal spacings of the resulting complexes are larger than that of original FeOCl by 0.51 to 0.68 nm as indicated in Table II.

Analytical values of IVC and IFC are as follows: IVC, C 15.0%, H 1.3%; IFC, C 14.1%, H 1.6%. These values resulted in the chemical formula of FeOCl (2-vinyl pyridine)$_{0.23}$ and FeOCl (furfural)$_{0.36}$. Kanamaru *et al.* [2] reported that the amount of the intercalated pyridine with FeOCl changed with reaction temperature, i.e., FeOCl (pyridine)$_{0.33}$ above 333 K and FeOCl (pyridine)$_{0.25}$ below 333 K.

IAC decomposed into an amorphous solid after being allowed to stand in air for 2 days. Therefore, it was not used for further heat-treatment.

3.2. Thermal degradation of the complexes

After heating to 423 K, both IVCs with and without γ-radiation changed into an amorphous solid regardless of heating in the ampoule or under nitrogen gas. Therefore, IVCs were not used for heat-treatment at higher temperatures. As a result, the thermal stabilities of the complexes increased in the order IFC > IVC > IAC.

TABLE II Basal spacings and molar ratios of FeOCl and the complexes

	Spacings (nm)	Δd (nm)	Molar ratio	
			FeOCl	Organic compound
FeOCl	0.79	–	1	–
IVC	1.30	0.51	1	0.23
IFC	1.40	0.61	1	0.36
IAC	1.47	0.68	1	–

Table III summarizes the thermal degradation products of FeOCl and IFCs with and without γ-radiation. FeOCl changed into Fe_2O_3 at 673 K and its degree of formation increased with increasing temperature. FeOCl was degradated preferentially in the ampoule rather than under nitrogen gas, but γ-radiation had no essential effect on the thermal degradation behaviour of IFC.

On heating to 423 K, the non-irradiated IFC changed slightly into some compound and simultaneously, the (0 1 0)-value of the remaining IFC decreased from 1.40 to 1.20 nm. An analogous compound also formed in IFCs, with and without γ-radiation, heated at 773 K in larger amounts. Table IV shows the X-ray diffraction data of this compound, $FeCl_2$ and hydrated $FeCl_2$. It is reasonable to conclude that the compound formed in IFCs is hydrated $FeCl_2$. Further, in view of the strong hygroscopy of $FeCl_2$, it may be reasonable to consider that $FeCl_2$ formed at the heating stage and then reacted with H_2O in air to result in the hydrated $FeCl_2$ after removal from the ampoule.

After heating IFC in the ampoule to 573 K, an unidentified compound, X, was detected in addition to Fe_2O_3 and the hydrated $FeCl_2$. Compound X never formed above 673 K, and Fe_3O_4 formed in larger amounts with increasing temperature. The radiated IFC exhibited a similar thermal degradation behaviour to that of the non-irratiated IFC. Compared with the non-irradiated IFC, however, compound X formed more favourably in the radiated IFC, especially in the ampoule. In order to convert IFC into compound X more completely, the γ-radiated IFC in the ampoule was heated at 598 K for 0.5 h. Only three peaks appeared in its X-ray diffraction profile. These were a strong peak at 19.6° (0.57 nm) and two weak peaks at 61.5° (0.190 nm) and 86.1° (0.142 nm) which are thought to be the first, third and fourth diffraction peaks from a layered structure. Analytical values of this compound are: C 11.4%, H 1.8%, Fe 40.3% and the difference 46.6%.

TABLE III Degradation products of FeOCl and IFCs with and without γ-radiation

HTT (K)	FeOCl		IFC		γ-IFC	
	N_2	Ampoule	N_2	Ampoule	N_2	Ampoule
423	FeOCl	FeOCl	IFC $FeCl_2$*†	IFC $FeCl_2$*	IFC	IFC $FeCl_2$*
573	FeOCl	FeOCl	$FeCl_2$ Fe_3O_4	$FeCl_2$ X Fe_3O_4*	$FeCl_2$ X Fe_3O_4*	X Fe_3O_4*
673	FeOCl	FeOCl Fe_2O_3	$FeCl_2$ Fe_3O_4	$FeCl_2$ Fe_3O_4	$FeCl_2$ Fe_3O_3 X*	X Fe_3O_4*
773	Fe_2O_3 Fe_3O_4	Fe_2O_3 FeOCl	Fe_3O_4 $FeCl_2$	Fe_3O_4 $FeCl_2$	Fe_3O_4 $FeCl_2$*	Fe_3O_4 $FeCl_2$ X*

* A small degree of formation.
† $FeCl_2$ or hydrated $FeCl_2$.

4. Discussion

Based on the results given above, the three possibilities described in the introduction are discussed below.

(i) On the contrary to montmollironite, the layered structure of FeOCl became unstable by intercalating with organic compounds. A lower-order oxidation product, Fe_3O_4, formed on heating IFC, rather than a higher-order oxidation product, Fe_2O_3, and Fe_3O_4 for FeOCl. Therefore, the lowering of the thermal stability by intercalating may be attributable to the removal of oxygen in the FeOCl layer by intercalating organic compounds or their derivatives at the heating stage. As the result, *the thermal stability of the layered structure of an inorganic compound is influenced in various ways by intercalating with an organic compound.*

The thermal stabilities of the complexes prepared here increased in the order IFC > IVC > IAC. This order does not necessarily coincide with the order of the (0 1 0)-values of the complexes. The stabilities of these complexes may be controlled more strongly by other factors, e.g. the reducing power of the intercalated organic compound or its derivatives at the heating stage.

(ii) All the degradation compounds, except for X, were identified using ASTM cards. As suggested from the analytical values, the unidentified compound X must be a layer-type complex with no

TABLE IV X-ray diffraction data of $FeCl_2$ and its related compounds

$FeCl_2$		$FeCl_2 \cdot 2H_2O$		$FeCl_2 \cdot 4H_2O$		IFC 773 K (in ampoule)		γ-IFC 773 K (in N_2)	
d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
0.59	63	0.5548	100	0.550	85	0.550	100	0.5578	100
				0.533	80				
				0.439	30				
		0.4281	75	0.436	16			0.4306	10
				0.397	100	0.397	65		
				0.348	25	0.347	23		
				0.343	10				
0.307	30			0.301	65	0.301	75		
		0.2884	45						
		0.2773	45	0.2777	45	0.2779	58	0.2772	22
		0.2763	90						
		0.2657	25	0.2663	16				
				0.2621	10				
				0.2197	40	0.2198	54		
				0.2182	40	0.2186	44		
		0.2141	35						
				0.2129	35	0.2130	31		

stoichiometric compositions. The kinds of the degradation product were strongly influenced by intercalating with organic compounds, e.g. $FeCl_2$ never formed in FeOCl but did in IFC. This phenomenon may be attributable to the preferential removal of oxygen in the FeOCl layer by the intercalated organic compounds.

(iii) In this work, there was no possibility of preparing the layer-type complex consisting of FeOCl and carbon, because a too-low thermal stability of the FeOCl layer itself to carbonize the intercalating organic compounds.

References

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