

Table I. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds (Continued)

Compound	Physical State	Chemical Shift, p.p.m.	Spin-Spin Splitting	
			No. peaks	Coupling constant, c.p.s.
$(\text{NaO})_3[\text{PONH}]_3$	In water	+1.5
$(\text{C}_2\text{H}_5\text{O})_3[\text{PONC}_2\text{H}_5]_3$	In CCl_4	-5.3
$(\text{KO})_4[\text{PONH}]_4$	In water	+3.7
Phosphonitrilic derivatives				
$[\text{PN}(\text{OC}_2\text{H}_5)_2]_3$	In CHCl_3	-17.9
$[\text{PN}(\text{OC}_2\text{H}_5)_2]_4$	Liquid	+0.6
$[\text{PN}(\text{NCS})_2]_3$	In CCl_4	+26.8
$[\text{PN}(\text{NCS})_2]_4$	In CCl_4	+49.1
$[\text{PN}[\text{NHC}(\text{S})\text{NH}_2]_2]_3$	In methanol	+10.8
$[\text{PN}[\text{NHC}(\text{S})\text{NH}_2]_2]_4$	In methanol	+21.2
$[\text{PN}[\text{NHC}(\text{S})\text{NHC}_6\text{H}_5]_2]_3$	In DMF	+2.2
$[\text{PN}[\text{NHC}(\text{S})\text{NHC}_6\text{H}_5]_2]_4$	In DMF	+23.2
Miscellaneous P-N compounds				
$[\text{C}_6\text{H}_5\text{NHPNC}_6\text{H}_5]_2$	In CHCl_3	{ -113.6 -109.2
$[\text{C}_6\text{H}_5\text{NHP}(\text{O})\text{NC}_6\text{H}_5]_2$	In 1-M-2-P	+12

^a DME = dimethoxyethane. ^b THF = tetrahydrofuran. ^c DMF = dimethylformamide.
^d DMSO = dimethylsulfoxide. ^e 1-M-2-P = 1-methyl-2-pyrrolidinone.

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Solid State Reaction Study of Hydrated Iron Oxide with Hydrated Nitrates of Nickel and Cobalt

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Pure $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and pure $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were heated with hydrated iron oxide at 315–1200° C. Dehydration was complete at 315° C. In the Ni experiments, NiFe_2O_4 was formed at 480° C. At 650° C., NiFe_2O_4 was the major constituent. In the Co experiments, CoFe_2O_4 did not form at 480° C., but appeared as the major constituent at 650° C. Both reactions were complete at 1200° C.

THE NEED CONTINUES for a better understanding of the transformation and reactions that occur in the preparation and application of catalysts and catalyst carriers. Chemical and physical changes occurring in mixtures of hydrated iron oxide with hydrated nitrates of nickel and cobalt are of both academic and industrial importance.

Similar information of the solid state reaction study of hydrated and α -aluminas with the hydrated nitrates of nickel and cobalt has been reported (4). In the nickel experiments, nickel aluminate was formed at 870° C. with hydrated alumina but not with α -alumina. At 1200° C. nickel aluminate was formed in each case, but to a lesser extent with α -alumina. In the cobalt experiments, cobalt

aluminate was formed at the same temperatures as the nickel compounds, but in slightly greater amounts.

Nickel ferrite has been prepared by solid state reaction between coprecipitated hydroxides of ferric iron and nickel at 1400°C. in an oxidizing atmosphere (3). Similarly, cobalt ferrite has been reported to result from the fusion of coprecipitated hydrates of cobalt and iron (1).

This report is concerned with the transformation and reactions that occur when a hydrated iron oxide ($\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) mixed separately with the hydrated nitrates of nickel and cobalt is calcined in air at various temperatures ranging from 315° to 1200° C.

APPARATUS AND TECHNIQUE

A narrow x-ray source Geiger-counter Norelco diffractometer, employing cobalt $K\alpha$ radiation at 45 Kv. and 10 ma. was used with a rotating flat specimen holder. The sample holder is circular and slips into a rotating device located in the position occupied by the usual stationary sample holder. The sample (<400 mesh) is rotated around an axis perpendicular to the irradiated surface at approximately 80 r.p.m. The goniometer was operated at $\frac{1}{2}^\circ$ per minute and the chart speed was 30 inches per hour. High precision divergence slit (1°) and receiving slit (0.006 inch) was used.

Relative intensities were measured by a comparison of peak heights. In cases where the peaks extended beyond the chart paper, peak widths at a given height from the base line were compared.

X-ray evaluations were made using the following standard patterns: nickel oxide, cobalto-cobaltic oxide, α -ferric oxide, α -ferric oxide monohydrate, nickel ferrite, and cobalt ferrite (1).

PREPARATION OF MATERIALS

Chemicals. Cobalt nitrate hexahydrate, analytical reagent, J.T. Baker Chemical Co.

Nickel nitrate hexahydrate, analytical reagent, Mallinckrodt Chemical Co.

Yellow iron oxide ($\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), YO-2087, C.K. Williams Co., confirmed by weight loss and x-ray diffraction pattern. The oxide contained 0.34 per cent sulfur.

Procedure. One mole of hydrated nitrate (nickel nitrate hexahydrate and cobalt nitrate hexahydrate used separately) is mixed with 1 mole of hydrated iron oxide by grinding in a mortar. Sufficient demineralized water is added to make a paste and mixing is continued for 15 minutes. The mix is dried in an oven, then calcined in air for 16 to 20 hours at temperatures ranging from 315° to 1200° C.

DISCUSSION

The calcination products of the 1 to 1 molar mixture of hydrated nitrates with α -ferric oxide monohydrate are given in Table I.

Table I. Calcination Products of the 1 to 1 Molar Mixture of Hydrated Nitrates with Hydrated Ferric Oxide

Time, Hours	Temp., ° C.	Compounds Identified	
		Ni(NO ₃) ₂ ·6H ₂ O- $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Co(NO ₃) ₂ ·6H ₂ O- $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
16	315	NiO ^a $\alpha\text{-Fe}_2\text{O}_3$	Co ₃ O ₄ $\alpha\text{-Fe}_2\text{O}_3$
16	480	NiO $\alpha\text{-Fe}_2\text{O}_3$ NiFe ₂ O ₄	$\alpha\text{-Fe}_2\text{O}_3$ Co ₃ O ₄
15-16	650	NiFe ₂ O ₄ NiO $\alpha\text{-Fe}_2\text{O}_3$	CoFe ₂ O ₄ $\alpha\text{-Fe}_2\text{O}_3$ Co ₃ O ₄
16	870	NiFe ₂ O ₄ NiO $\alpha\text{-Fe}_2\text{O}_3$	CoFe ₂ O ₄ $\alpha\text{-Fe}_2\text{O}_3$ Co ₃ O ₄
16	1200	NiFe ₂ O ₄	CoFe ₂ O ₄

^a Major constituent listed first.

Dehydration is complete at 315° C. Small amounts of nickel ferrite form at 480° C. whereas clear cut x-ray diffraction evidence for cobalt ferrite first appears at 650° C. The nickel and cobalt series are similar in that the ferrite is the major constituent after a calcination temperature of 650° C. and some temperature higher than 870° C. is needed before reaction is complete.

Cobalto-cobaltic oxide peaks are much smaller than expected at 870° C. and to a lesser extent at the lower temperatures. Crystalline cobalto-cobaltic oxide appears to be present in an attenuated state.

Past work (4) covering similar type calcinations of 1 to 1 molar mixtures of hydrated nickel and cobalt nitrates with α -alumina and hydrated alumina show that the formation of aluminates is not complete at 1200° C. A more rapid and complete solid state reaction is obtained when α -ferric oxide monohydrate is substituted for the different aluminas.

Nickel ferrite and cobalt ferrite have the spinel-type structure (6) which has also been reported for the aluminates of nickel and cobalt (2, 5).

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