Thermal Studies of Nickel, Cobalt, Iron, and Copper Oxides and Nitrates

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Thermogravimetric analysis (TGA) studies of cobalt nitrate hexahydrate, cupric nitrate trihydrate, ferric nitrate nonahydrate, and nickel nitrate hexahydrate were made in air from 20° to 1040° C. at a programming rate of approximately 5–6° C. per minute. Extended runs at lower temperatures in air were also conducted. The importance of time in the decomposition of hydrated nitrates was demonstrated. TGA technique indicated the existance of a stable nickel basic nitrate containing about 1.5 moles of water at 210° C. No intermediate compounds were found during the decomposition of the hydrated nitrates of cobalt, copper, and iron. Reversible decomposition of cobalto-cobaltic oxide to cobaltous oxide and oxygen at 1000–1010° C. was observed. Differential thermal analysis study of the reduction of nickel oxide indicated the transition of nickel oxide from a slightly distorted (rhombohedral) variant of the rock salt structure to the rock salt structure. The reversibility of the phase transition at 250° C. was demonstrated. Reduction of nickel oxide was related to the 250° to 400° C. exotherm. Observation of a reversible transition of α-nickel to β-nickel at 360° C. was made. No heat effects were detected above 400° C.

THE DECOMPOSITION of the nitrates of nickel, cobalt, iron, and copper and the reduction of nickel oxide have important applications in catalyst manufacture. Crystallite size and per cent reduction and many other physical and chemical properties are frequently related to the temperature and time of calcination and reduction. Catalyst specifications are dependent on applications, necessitating varied treatment which in turn requires a thorough understanding of the physical and chemical properties.

The transition of nickel nitrate hexahydrate to the trihydrate has been observed at temperatures as low as 55° C. (*6*); after a period of rapid weight loss, a break in the decomposition curve was detected at 205° C. The composition of the curve in this region was reported to correspond approximately to anhydrous nickel nitrate (*9*). Kirk and Othmer (*4*) reviewed the decomposition of cobalt nitrate hexahydrate to cobalt nitrate trihydrate at 70–74° C. The trihydrate has not been dehydrated without decomposition. Similarly, the anhydrous salt of ferric nitrate nonahydrate has not been prepared. In the case of the decomposition of cupric nitrate trihydrate, the anhydrous salt was not prepared since an oxynitrate formed before all the water was driven off (*8*). Chufarov (*2*) observed that cobalto-cobaltic oxide decomposes to cobaltous oxide at 950° C. in a nitrogen atmosphere.

Mellor (*6*) covered the work of many investigators and their conditions for studying the reduction of nickel oxide. A temperature as low as 118–120° C. was reported by Gallo (*3*) to be sufficient for reduction. Water reportedly slows the reaction. Rooksby (*7*) reported a structural change of nickel oxide above about 200° C. to a rock salt form. Below this temperature nickel oxide has a slightly distorted (rhombohedral) variant of the rock-salt structure. Kubaschewski and Evans (*5*) have listed a transition of nickel metal from the α to β form at 357° C.

This report is concerned with a thermogravimetric study (TGA) of the nitrates and oxides of nickel, cobalt, iron, and copper in air from 20° to 1040° C. at a programming rate of approximately 5–6° C. per minute. Extended runs at lower temperatures in air were also conducted. A differential thermal analysis (DTA) study was made of the reduction of crystalline nickel oxide. X-ray diffraction studies were correlated with TGA and DTA results.

APPARATUS AND TECHNIQUE

A Stanton Model TR-1 thermobalance was employed for the weight loss studies. The temperature of the thermogravemetric analysis balance was either programmed to 1040° C. at a rate of approximately 5–6° C. per minute or held for a given time at a lower level. The instrument consists of a beam-type balance, one arm of which is modified to allow the positioning of the sample in the center of the furnace. A Pt *vs.* Pt + 13% Rh thermocouple is located adjacent to the crucible containing the sample. Weight change is limited neither by the range of chart nor by the range of a single beam deflection. Advantage is taken of the servo-driven mechanism to operate electric weight loading at the end of each full beam movement. By this means it is possible to follow weight change up to 1 gram automatically with a sensitivity of 1 mg. The maximum rate of weight change is 400 mg. per minute.

The R.L. Stone differential thermal analysis equipment, Model DTA-1OMC, was used for the nickel oxide reduction. The temperature was programmed to 1000° C. at a rate of 5° C. per minute. A water cooled-type furnace surrounds the sample holder. A large dome is placed over the furnace for controlled atmosphere work. A 0.2–0.3-ml. sample (< 400 mesh) and a comparison material (α-alumina, prepared by calcining Filtrol hydrated alumina for 24 hours at 1260° C., and confirmed by x-ray diffraction) are positioned in adjacent openings, at the upper end of gas flow tubes, located near the top of the sample head. Hydrogen is passed through the sample and the comparison material at the same rate. Differential temperature (Pt + 10% Rh; Pt; Pt + 10% Rh thermocouple) and reference temperature (Pt *vs.* Pt + 10% Rh thermocouple) are transmitted to different recorders.

A narrow x-ray source Geiger-counter Norelco diffractometer, employing copper $K\alpha$ radiation at 45 kv. and 20 ma. and 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 0.5° per minute, and the chart speed was 30 inches per hour. High precision divergence slit (1°) and receiving slit (0.006 inch) was used.

Table I. TGA Results in Air

Programmed Run		Theoretical Wt. Loss		Extended Run			
					Time[a]		
Temp., °C.	% Wt. loss	Loss of	% Wt. loss	Temp., °C.	Hr.	Min.	% Wt. loss
			$Ni(NO_3)_2 \cdot 6H_2O$[b]				
50	0.0	H_2O	6.2	20-100	0	46	3.3
100	2.0	$2H_2O$	12.4	100-150	1	50	9.3
150	2.2	$3H_2O$	18.6	150-200	5	5	24.6
200	7.4	$4H_2O$	24.8	200	11	40	28.8
250	22.4	$5H_2O$	31.0	200-210	12	30	29.5
300	39.0	$6H_2O$	37.2	210	23	47	42.1
350	52.1	$6H_2O,2N,5O$[c]	74.3	210-220	23	52	42.1
400	73.9			220	24	37	42.1
750	74.1			220-250	24	41	42.2
1040	74.2			250	26	38	42.4
				250-300	26	47	42.4
				300	49	17	71.9
				300-350	49	26	71.9
				350	54	51	73.1
				350-400	55	0	73.1
				400	57	24	73.3
				400-450	57	33	73.3
				450	77	36	74.2
			$Co(NO_3)_2 \cdot 6H_2O$[d]				
50	0.0	H_2O	6.2	20-100		35	3.4
100	0.3	$2H_2O$	12.4	100-150	1	26	21.6
150	3.2	$3H_2O$	18.6	150-200	4	11	38.2
200	11.6	$4H_2O$	24.8	200	4	51	41.7
250	27.2	$5H_2O$	31.0	200-210	6	56	52.8
300	40.4	$6H_2O$	37.1	210	26	54	71.1
350	70.6	$6H_2O,2N,4\frac{2}{3}O$[e]	72.4	210-250	27	5	71.1
700	72.2			250	29	45	71.6
1000	72.2			250-300	29	54	71.7
1010	74.0			300	33	21	71.9
1000	72.2			300-350	33	29	72.1
1010	74.0			350	52	46	72.3
			$Fe(NO_3)_3 \cdot 9H_2O$[f]				
50	0.0	H_2O	4.5	20-100	0	20	1.2
100	0.0	$2H_2O$	8.9	100-150	1	10	28.0
150	6.5	$3H_2O$	13.4	150-200	3	26	76.4
200	29.6	$4H_2O$	17.8	200-215	7	26	77.2
250	75.3	$5H_2O$	22.3	215	25	1	79.0
300	77.8	$6H_2O$	26.8	215-250	25	9	79.0
350	79.8	$7H_2O$	31.2	250	31	56	79.3
1000	80.0	$8H_2O$	35.7	250-300	32	5	79.3
1030	80.0	$9H_2O$	40.1	300	33	51	79.5
		$9H_2O,3N,7\frac{1}{2}O$[g]	80.2	300-350	34	0	79.5
				350	64	20	79.9
				350-400	64	28	79.9
				400	82	31	80.1
				400-450	82	41	80.1
				450	83	37	80.1
			$Cu(NO_3)_2 \cdot 3H_2O$[h]				
50	0.0	H_2O	7.5	20-100	0	31	0.1
100	0.0	$2H_2O$	14.9	100-150	1	26	9.7
150	0.7	$3H_2O$	22.4	150-200	3	51	43.5
200	4.9	$3H_2O,2N,5O$[i]	67.1	200	4	26	44.8
250	24.7			200-210	6	1	47.6
300	43.5			210	52	46	66.4
350	65.5			210-250	52	52	66.9
400	67.0			250	54	52	66.9
1000	67.0			250-300	55	1	67.0
1040	67.0			300	78	34	67.0
				300-350	78	43	67.0
				350	79	13	67.0

[a] Time is cumulative. The time at a given condition is obtained by subtracting the preceeding time from the time under consideration [b] 5.4° C./min. [c] This assumes NiO is the final product. [d] 5.8° C./min. [e] This assumes Co_3O_4 is the final product. A theoretical weight loss 74.3% corresponds to a final product of CoO. [f] 5.6° C./min. [g] This assumes α-Fe_2O_3 is the final product. [h] 5.7° C./min. [i] This assumes CuO is the final product. A theoretical weight loss of 70.4% corresponds to a final product of Cu_2O.

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

CHEMICALS

Cobalt nitrate hexahydrate (Mallinckrodt Chemical Works), copper (II) nitrate trihydrate (Allied Chemical & Dye Corp.), and iron (III) nitrate nonahydrate (Allied Chemical & Dye Corp.) met ACS specifications. Nickel nitrate hexahydrate (J.T. Baker Chemical Co.) was reagent grade. Nickel oxide, prepared by calcining J.T. Baker nickel nitrate hexahydrate for 16 hours at 1800° F., was confirmed by x-ray diffraction.

DISCUSSION

There was no attempt in the programmed thermogravimetric analysis studies to dehydrate the various nitrates without complete decomposition. However, extended runs do allow opportunities for the detection of intermediate decomposition compounds. Table I presents a TGA demonstration of the importance of time in the decomposition of hydrated nitrates. Nickel nitrate hexahydrate loses slightly more than 1 mole of water at 200° C. in the programmed run. A temperature of approximately 400° C. is needed before complete decomposition to nickel oxide occurs (Figure 1). The weight loss is moderately uniform, and the red-brown fumes of nitrogen dioxide appear before a temperature of 250° C. is obtained. This suggests that compound decomposition occurs before 4 moles of water are dehydrated. The experiment was not conducted to determine if nitrogen dioxide resulted directly from decomposition. A considerably slower heat-up as exhibited in the extended run results in decomposition occurring at lower temperatures. The application of the TGA technique indicates the existence of a compound of nickel stable at 210° C. when the temperature is approached in the manner presented in Table I. The weight loss at 210° C. corresponds closely to what would be experienced if a nickel basic nitrate containing about 1.5 moles of water were formed. Wendlandt (*9*) detected a compound having the approximate composition of anhydrous nickel nitrate at 205° C. However, the observation of red-brown nitrogen dioxide fumes at temperatures both below and above 210° C. suggests that the presence of anhydrous nickel nitrate is unlikely.

Table I also shows a programmed run for cobalt nitrate hexahydrate indicating that approximately complete decomposition occurs at about 350° C. The extended run suggests that 150° C. is sufficient to dehydrate 3 moles of water and start the decomposition of the nitrate. Red-brown fumes of nitrogen dioxide are observed. Complete decomposition occurs at about 210° C. The cobalt nitrate hexahydrate does not attain constant weight at any stage before complete decomposition to cobalto-cobaltic oxide. At 1000–1010° C., a reversible weight change is observed which corresponds to the decomposition of cobalto-cobaltic oxide to cobaltous oxide and oxygen. This repeated detection of the reversible decomposition in air by TGA technique presents a temperature where catalytic performance would be expected to change.

In the case of ferric nitrate nonahydrate, decomposition to α-ferric oxide is approaching completeness at approximately 250° C. in the programmed experiment and about 200° C. in the extended run. This compound is unique in that decomposition occurs without the detection of red-brown fumes of nitrogen dioxide. If nitrogen dioxide is formed, it may react with the excess of water vapor to produce nitric acid and nitric oxide.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

There is no evidence for the intermediate stable compound.

For cupric nitrate trihydrate, the decomposition to cupric oxide is essentially complete at 350° C. in the programmed run and at 210° C. in the extended run. Nitrogen dioxide is detected in both runs. There is no evidence for the formation of an oxynitrate as has been previously reported in the literature (*8*, *9*). This again demonstrates the importance of time, surface availability, particle size and other physical properties in relation to compound breakdown and subsequent catalyst performance.

X-ray diffraction data for the various samples studied by TGA and the sample that was calcined to obtain nickel oxide employed in the reduction study are shown in Table II. Any reversible structural changes or dissociation reactions would not be detected by pattern evaluation.

Table II. X-Ray Diffraction Data

Sample Description	Diffraction Data
$Ni(NO_3)_2 \cdot 6H_2O$, TGA in air from 20° to 1040° to 20° C.	NiO
$Co(NO_3)_2 \cdot 6H_2O$, TGA in air from 20° to 1010° to 20° C.	Co_3O_4
$Fe(NO_3)_3 \cdot 9H_2O$, TGA in air from 20° to 1030° to 20° C.	αFe_2O_3
$Cu(NO_3)_2 \cdot 3H_2O$, TGA in air from 20° to 1040° to 20° C.	CuO
$Ni(NO_3)_2 \cdot 6H_2O$, calcined 19 hours at 996° C.	NiO

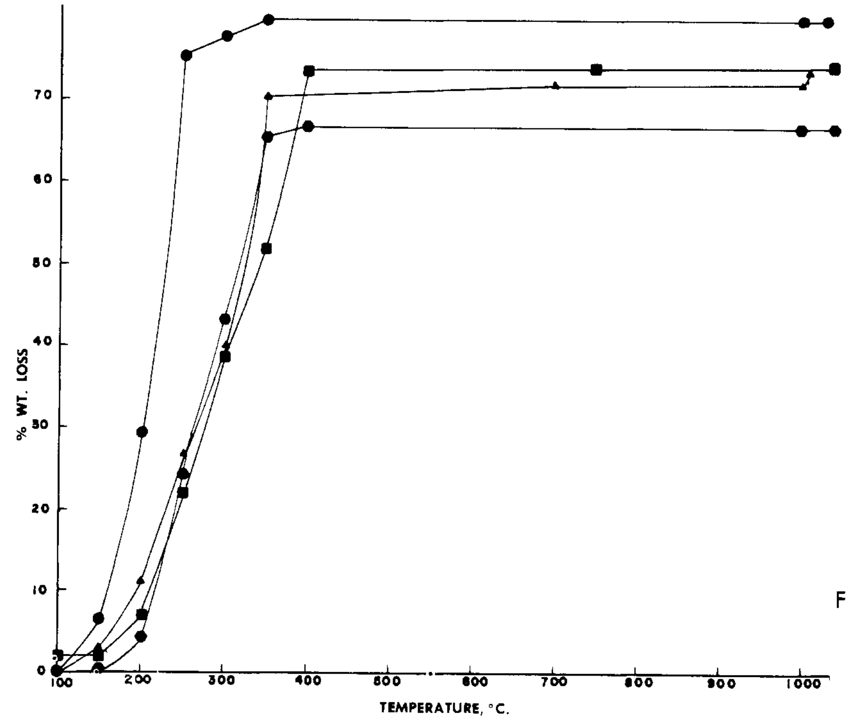

Figure 1. TGA curves for the hydrated nitrates in air

■ $Ni(NO_3)_2 \cdot 6H_2O$

▲ $Co(NO_3)_2 \cdot 6H_2O$

● $Fe(NO_3)_3 \cdot 9H_2O$

● $Cu(NO_3)_3 \cdot 3H_2O$

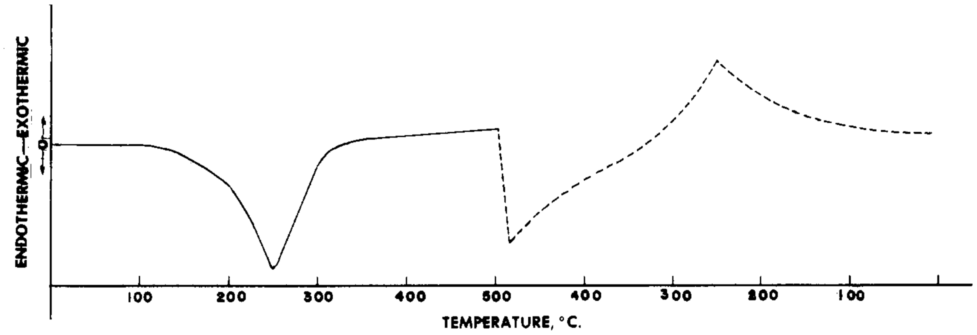

Figure 2. Reduction of Nickel Oxide

—— Heating curve
- - - - Cooling curve
Atm. pressure
H_2 flow, 10,000 SV.
Heating rate, 5° C./min. to 1000° C.
Cooled under H_2 flow

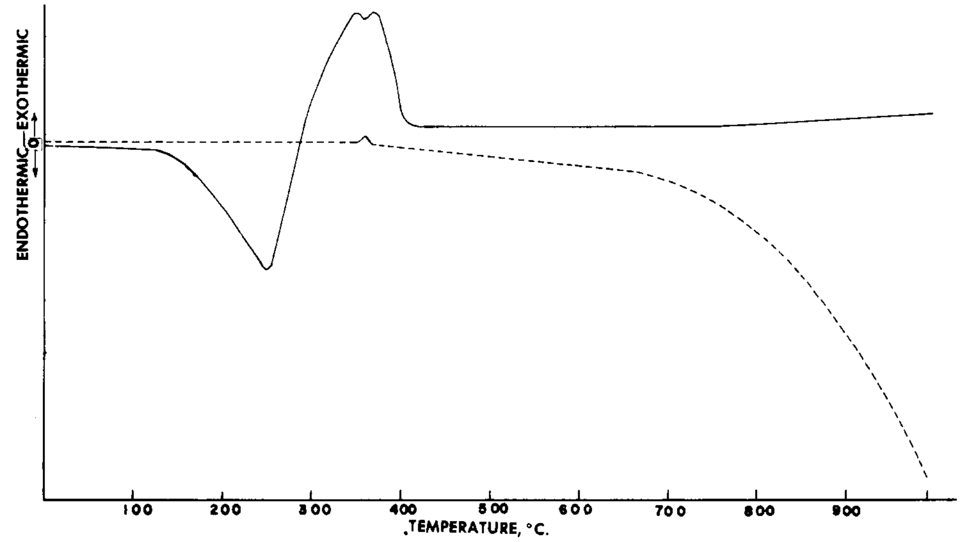

Figure 3. DTA Curve for nickel oxide in air

—— Heating curve
- - - - Cooling curve
Atm. pressure
Air flow, 10,000 SV.
Heating rate, 5° C./min. to 500° C.
Cooled under air flow

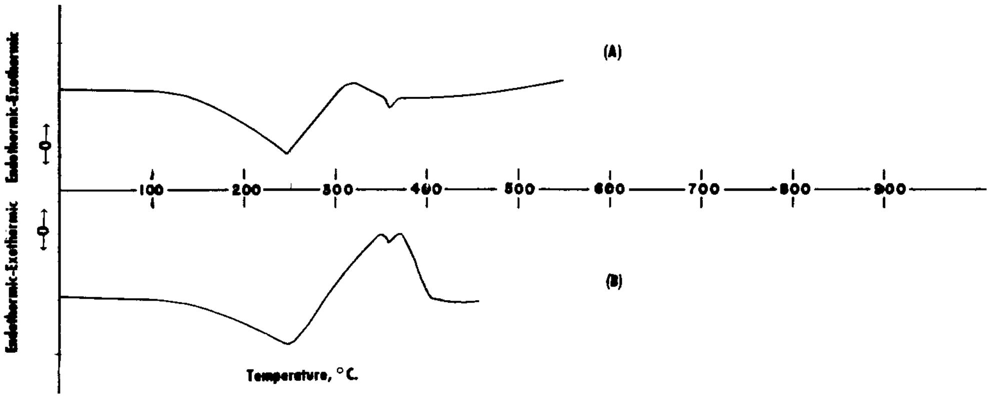

Figure 4. Nickel oxide reduction

(A) Atm. pressure
H_2 flow (20°–250° C.), 10,000 SV.
He flow (250°–550° C.), 10,000 SV.
Heating rate, 5° C./min. to 550° C.
(B) Atm. pressure
H_2 flow, 10,000 SV.
Heating rate, 5° C./min. to 450° C.

The differential thermal analysis technique is used to obtain a qualitative look at the heat effects involved during the reduction of crystalline nickel oxide. There is an endothermic trend with an apex at approximately 250° C. (Figure 2). Thermodynamic data (−0.3 Kcal. per mole at 250° C.) indicate that the reduction of nickel oxide is slightly exothermic. DTA evidence that this peak is associated with the transition of nickel oxide—from a slightly distorted (rhombohedral) variant of the rock salt structure to the rock salt structure—is demonstrated in Figure 3, where the pattern for nickel oxide in air exhibits a similar endothermic peak. In addition, the DTA study presents evidence for the reversibility of this phase change at 250° C. Figure 2 contains an exothermic region from 250° to 400° C. which is related to the reduction of nickel oxide. Switching from hydrogen to helium during the reduction (at 250° C.) practically eliminates the exothermic region (Figure 4).

This work clearly identifies a small reversible endothermic peak at 360° C. which undoubtedly represents the transition of α-Ni to β-Ni. It is of considerable catalytic importance to note that no heat effects were observed above 400° C.

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