Solid State Reaction Study of Chromium Trioxide and Chromium(ic) Oxide with the Hydrated Nitrates of Nickel and Cobalt

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Pure $Ni(NO_3)_2 \cdot 6H_2O$ and pure $Co(NO_3)_2 \cdot 6H_2O$ were heated separately with CrO_3 and with Cr_2O_3 for 16 hours at 260° to 1200° C. Dehydration was complete at 260° C. In the Ni experiments, $NiCr_2O_4$ was formed at 650° C. with CrO_3 and at 870° C. with Cr_2O_3. In the Co experiments, $CoCr_2O_4$ was formed at 480° C. with CrO_3 and at 650° C. with Cr_2O_3. Chromites are present in appreciable concentration at 1200° C., but only in the case of the Co–CrO_3 mixture is the reaction complete.

THE decompositions, transformations, and reactions that occur in the preparation and application of catalysts and catalyst carriers are continually being investigated, reviewed, and expanded. Solid state reactions involving chromium trioxide and chromium(ic) oxide with the hydrated nitrates of nickel and cobalt are academically important and also serve to promote a better industrial understanding of catalysts involved in hydrogenation, selective hydrogenation, and dehydrogenation processes.

Past work reported the solid state reaction study of hydrated and α-aluminas with the hydrated nitrates of nickel and cobalt (*5*). Other related solid state studies includes mixtures of hydrated iron oxide with the hydrated nitrates of nickel and hydrated nitrates of cobalt heated at 315° to 1200° C. (*3*).

Cobalt chromite has been reported to form by precipitating a mixed solution of equimolar parts of chrome-alum and cobalt chloride with sodium carbonate; nickel chromite was also reported by a process analogous to that used for the cobalt salt (*4*). Fischbeck and Einecke prepared nickel chromite and cobalt chromite by sintering mixtures of their component oxides (*2*).

This report is concerned with the decompositions, transformations, and reactions that occur when chromium trioxide and/or chromium(ic) oxide mixed separately with the hydrated nitrates of nickel and cobalt is calcined in air at various temperatures ranging from 260° to 1200° C. Most catalyst preparation techniques will be covered by this temperature range.

EXPERIMENTAL

Reagents. One mole of hydrated nitrate (nickelous nitrate hexahydrate and cobaltous nitrate hexahydrate, Baker & Adamson Quality, Allied Chemicals, used separately) is mixed with 2 moles of chromium trioxide (J. T. Baker Chemical Co.) and with 1 mole of chromium(ic) oxide (separately) by grinding in a mortar. Chromium(ic) oxide is prepared by calcining chromium trioxide for 16 hours at 650° C., then confirmed by x-ray diffraction. 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 for 16 hours at temperatures ranging from 260° to 1200° C.

Apparatus and Procedure. A narrow x-ray-source Geiger-counter Norelco diffractometer employing Cu Kα radiation at 45 kv. and 20 ma. and Co Kα 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. Rotation is introduced to provide relative intensity measurements of higher accuracy and to reduce any possible orientation effects. 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) were 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.

Table I. Calcination Products of the 1-to-2 Molar Mixture of Nickelous Nitrate Hexahydrate with Chromium Trioxide and the 1-to-1 Molar Mixture of Nickelous Nitrate Hexahydrate with Chromium(ic) Oxide

Calcination time—16 hours

	Compounds Identified	
Temp., ° C.	$Ni(NO_3)_2 \cdot 6H_2O$–$2CrO_3$	$Ni(NO_3)_2 \cdot 6H_2O$–Cr_2O_3
260	γ-NiOOH[a] CrO_3 Cr_3O_8 NiO	Cr_2O_3, hexagonal NiO γ-NiOOH
480	NiO Cr_2O_3, hexagonal	NiO Cr_2O_3, hexagonal
650	$NiCr_2O_4$ (40%)[b] NiO Cr_2O_3, hexagonal	NiO Cr_2O_3, hexagonal
870	$NiCr_2O_4$ (80%) NiO Cr_2O_3, hexagonal	$NiCr_2O_4$ (50%) NiO Cr_2O_3, hexagonal
1200	$NiCr_2O_4$ (>95%) NiO Cr_2O_3, hexagonal	$NiCr_2O_4$ (80%) NiO Cr_2O_3, hexagonal

[a] The compounds are listed in the order of their concentration as per x-ray diffraction. [b] Percentage of constituent as per x-ray diffraction.

Table II. Calcination Products of the 1-to-2 Molar Mixture of Cobaltous Nitrate Hexahydrate with Chromium Trioxide and the 1-to-1 Molar Mixture of Cobaltous Nitrate Hexahydrate with Chromium(ic) Oxide

Calcination time—16 hours

	Compounds Identified	
Temp., ° C.	$Co(NO_3)_2 \cdot 6H_2O\text{-}2CrO_3$	$Co(NO_3)_2 \cdot 6H_2O\text{-}Cr_2O_3$
260	CrO_3[a] Cr_3O_8 Co_3O_4 (?)	Cr_2O_3, hexagonal Co_3O_4
480	$CoCr_2O_4$ (80%)[b] Cr_2O_3, hexagonal Co_3O_4	Cr_2O_3, hexagonal Co_3O_4
650	$CoCr_2O_4$ (> 90%) Cr_2O_3, hexagonal Co_3O_4	Cr_2O_3, hexagonal Co_3O_4 $CoCr_2O_4$ (30%)
870	$CoCr_2O_4$ (> 97%) Cr_2O_3, hexagonal Co_3O_4	$CoCr_2O_4$ (80%) Cr_2O_3, hexagonal Co_3O_4
1200	$CoCr_2O_4$	$CoCr_2O_4$ (> 90%) Cr_2O_3 Co_3O_4

[a] The compounds are listed in the order of their concentration as per x-ray diffraction. [b] Percentage of constituent as per x-ray diffraction.

X-ray evaluations were made using the following standard patterns: nickel oxide, gamma-nickel hydroxide, nickel chromite, cobalto-cobaltic oxide, cobalt chromite, chromium trioxide, chromium(ic) oxide, and chromium oxide (Cr_3O_8) (*1*).

Calcinations were made by placing individual porcelain dishes in a static air furnace. Thermocouples were secured in the mix being calcined. Iron constantan thermocouples were used at 260° and 480° C., and chromel-alumel thermocouples were used at 650°, 870°, and 1200° C.

RESULTS AND DISCUSSION

The calcination products of the 1-to-2 molar mixture of nickelous nitrate hexahydrate with chromium trioxide and the 1-to-1 molar mixture of nickelous nitrate hexahydrate with chromium(ic) oxide are given in Table I.

There is a greater tendency for the nickel chromite to form using chromium trioxide than with chromium(ic) oxide. Nickel chromite forms at 650° C. when chromium trioxide is used whereas past work (*5*) shows that nickel aluminate does not form at 650° C.

Table II shows a similar study substituting cobaltous nitrate hexahydrate for nickelous nitrate hexahydrate.

The cobalt series shows a trend similar to the nickel series—that is, there is a greater tendency for cobalt chromite to form using chromium trioxide than with chromium(ic) oxide. Cobalt chromite is present in appreciable concentration at 480° C.; this was not the case for nickel chromite.

Table III. Calcination Products of Chromium Trioxide

Calcination time—16 hours

Temp., ° C.	Compounds Identified
260	Cr_3O_8
480	Cr_2O_3, hexagonal
650	Cr_2O_3, hexagonal
870	Cr_2O_3, hexagonal
1200	Cr_2O_3, hexagonal

Calcination studies at 260° C. indicated similar behavior of the chromium oxides in both the nickel and cobalt series. Cobalto-cobaltic oxide was the only oxide form of cobalt appearing, although its presence was questionable in the chromium trioxide study at 260° C.

In both the nickel and cobalt studies, the hexagonal chromia peaks at high temperatures are much smaller than expected. Crystalline hexagonal chromia is present in an attenuated state. This is quite frequently the case for hexagonal metal oxide at elevated temperatures.

A similar series of calcinations for unmixed chromium trioxide is presented in Table III.

There is no evidence for cubic Cr_2O_3 in this study. Chromium trioxide alone shows approximately the same transformation series as was observed for the nickel and cobalt mixtures with the exception of the 260° C. study. The mixtures contained some chromium trioxide. The effects of cobalt and nickel cannot be ruled out; however, the oxidizing characteristics of the oxides of nitrogen may retard the reduction of CrO_3 to Cr_3O_8 thus accounting for the difference.

LITERATURE CITED

(1) Am. Soc. Testing Materials, X-Ray Powder Data Cards, 4-0835, 6-0075, 4-0763, 9-418, 1-1122, 9-47, and 7-267, Philadelphia, Pa., 1963.

(2) Fischbeck, K., Einecke, E., *Z. anorg. allgem. Chem.* **167**, 21 (1927).

(3) Keely, W.M., Maynor, H.W., J. CHEM. ENG. DATA **9**, 170 (1964).

(4) Mellor, J.W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. **XI**, p. 204, Longmans, Green, New York, 1931.

(5) Pattison, J.N., Keely, W.M., Maynor, H.W., J. CHEM. ENG. DATA **5**, 433 (1960).

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