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

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Pure $Cu(NO_3)_2 \cdot 3H_2O$ and pure $Zn(NO_3)_2 \cdot 6H_2O$ were heated separately with CrO_3 and Cr_2O_3 for 16 hours at 260° to 1200° C. Mixtures of the hydrated nitrates of Cu and Zn were heated, also, with CrO_3 for 16 hours at 260° to 1200° C. In the Cu experiments, $CuCr_2O_4$ was formed at 480° C. in both the CrO_3 and Cr_2O_3 mixtures, but to a considerably greater extent in the CrO_3 mixtures. $Cu_2Cr_2O_4$ appears at 870° C. and is the major constituent at 1200° C. In the Zn experiments, $ZnCr_2O_4$ was formed at 480° C., in both the CrO_3 and Cr_2O_3 mixtures but, as was the case in the Cu study, to a greater extent in the CrO_3 mixtures. $ZnCr_2O_4$ formation was complete at 870° C. in the CrO_3 mixtures. The Cu-Zn-CrO_3 mixtures resulted in $ZnCr_2O_4$ and $CuCr_2O_4$ at 480° C. Zn completely displaces Cu in the chromite at 870° and 1200° C.

SOLID STATE REACTION STUDIES, involving chromium trioxide and chromium(ic) oxide with the hydrated nitrates of copper and zinc, add to the inorganic reaction literature and serve for a better knowledge of the phases existing in solid inorganic catalysts after different calcination treatments. Cuprous chromite has been reported by calcining cupric chromate in a crucible exposed to the reducing action of the furnace gases and extracting the product with hydrochloric acid. Cupric chromite was obtained by heating the cuprous salt in oxygen below 870° C. Zinc chromite has been reported to result by melting a mixture of chromic and zinc oxide with boric oxide in a porcelain oven and extracting the product with hydrochloric acid (*5*). Past solid state investigations contain studies of the hydrated nitrate of nickel and the hydrated nitrate of cobalt with hydrated alumina, α-alumina, hydrated iron oxide, chromium trioxide, and chromium(ic) oxide, separately, over temperature ranges extending from 260° to 1200° C. (*3, 4, 6*). 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 copper and zinc, are calcined in air at various temperatures ranging from 260° to 1200° C. Also, similar temperature studies are made for a chromium trioxide, cupric nitrate trihydrate, and zinc nitrate hexahydrate mixture. The temperature range employed covers a large majority of the calcinations frequently involved in catalyst preparations.

EXPERIMENTAL

Chemicals. Cupric nitrate trihydrate, reagent, Baker & Adamson Quality, Allied Chemical. Meets A.C.S. specifications. Assay ($Cu(NO_3)_2 \cdot 3H_2O$), minimum 99.5%.

Zinc nitrate hexahydrate, reagent, J. T. Baker Chemical Company. Assay ($Zn(NO_3)_2 \cdot 6H_2O$), 99.1%.

Chromium trioxide (CrO_3), reagent, J. T. Baker Chemical Company. Meets A.C.S. specifications. Assay (CrO_3), 99.8%.

Chromium(ic) oxide (Cr_2O_3), prepared by calcining chromium trioxide for 16 hours at 650° C., then confirmed by x-ray diffraction.

Preparation. One mole of hydrated nitrate—cupric nitrate trihydrate and zinc nitrate hexahydrate used separately—is mixed with two moles of chromium trioxide and with one mole of chromium(ic) oxide, separately, by grinding in a mortar. Also, 1 mole of cupric nitrate trihydrate, 1 mole of zinc nitrate hexahydrate, and 2 moles of chromium trioxide are mixed by grinding in a mortar. Sufficient demineralized water is added to make a paste and mixing is continued for 15 minutes. The various mixtures are oven dried, then calcined for 16 hours at temperatures ranging from 260° to 1200° C.

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.

Operations and Procedure. A narrow x-ray source Geiger-counter Norelco diffractometer, employing copper $K\alpha$ radiation at 45 kv. and 20 ma., was employed 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 ½° 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 instances 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: cupric oxide, zinc oxide, cupric chromite, cuprous chromite, zinc chromite, chromium trioxide, chromium(ic) oxide, and chromium oxide, Cr_3O_8 (*1*).

RESULTS AND DISCUSSION

Table I contains all calcination products. Copper chromite and zinc chromite exhibit a greater tendency to form when chromium trioxide is used in place of chromium(ic) oxide. This was also the case for the nickel and cobalt series previously reported (*3*). Compound formation is fre-

Table I. Calcination Products

Calcination time, 16 hours

Temp., °C.	Compounds Identified				
	$Cu(NO_3)_2 \cdot 3H_2O$-$2CrO_3$	$Cu(NO_3)_2 \cdot 3H_2O$-Cr_2O_3	$Zn(NO_3)_2 \cdot 6H_2O$-$2CrO_3$	$Zn(NO_3)_2 \cdot 6H_2O$-Cr_2O_3	$1Cu(NO_3)_2 \cdot 3H_2O$ $1Zn(NO_3)_2 \cdot 6H_2O$-$2CrO_3$
260	Cr_3O_8[a] CrO_3 CuO?	Cr_2O_3, hexagonal CuO	?	Cr_2O_3, hexagonal ZnO ?	ZnO CuO ?
480	$CuCr_2O_4$ (50%)[b] Cr_2O_3, hexagonal (25%) CuO (25%)	Cr_2O_3, hexagonal (45%) CuO (45%) $CuCr_2O_4$ (10%)	$ZnCr_2O_4$ (95%) Cr_2O_3, hexagonal ZnO	$ZnCr_2O_4$ (40%) ZnO (30%) Cr_2O_3, hexagonal (30%)	$ZnCr_2O_4$ $CuCr_2O_4$ CuO ZnO
650	$CuCr_2O_4$ (70%) Cr_2O_3, hexagonal (15%) CuO (15%)	Cr_2O_3, hexagonal (35%) CuO (35%) $CuCr_2O_4$ (30%)	$ZnCr_2O_4$ (97%) Cr_2O_3, hexagonal ZnO	$ZnCr_2O_4$ (85%) Cr_2O_3, hexagonal ZnO	$ZnCr_2O_4$ CuO ZnO $CuCr_2O_4$
870	$CuCr_2O_4$ (>90%) Cr_2O_3, hexagonal CuO, weak $Cu_2Cr_2O_4$, weak	$CuCr_2O_4$ (70%) Cr_2O_3, hexagonal CuO $Cu_2Cr_2O_4$	$ZnCr_2O_4$	$ZnCr_2O_4$ (>90%) Cr_2O_3, hexagonal ZnO	$ZnCr_2O_4$ CuO ZnO
1200	$Cu_2Cr_2O_4$ Cr_2O_3, hexagonal $CuCr_2O_4$ (>5%)	$Cu_2Cr_2O_4$ Cr_2O_3, hexagonal $CuCr_2O_4$ (>5%)	$ZnCr_2O_4$	$ZnCr_2O_4$ (>90%) Cr_2O_3, hexagonal ZnO	$ZnCr_2O_4$ CuO

[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.

quently enhanced when one of the reactants is undergoing decomposition.

The conversion of cupric chromite to cuprous chromite is demonstrated at 870° and 1200° C. in the copper series. Zinc chromite formation is complete at 870° C. in the chromium trioxide mixture.

Except for the cupric nitrate trihydrate—chromium(ic) oxide series—there are unexplained peaks in the x-ray diffraction patterns of the samples calcined at 260° C. These unexplained peaks may be associated with either unknown chromium-oxygen compounds or unknown reaction products.

The affinity of zinc as compared with copper for chromite formation is demonstrated in the study of the mixture consisting of 1 mole of cupric nitrate trihydrate, 1 mole of zinc nitrate hexahydrate, and 2 moles of chromium trioxide. This affinity of zinc over copper is most likely related to relative ionization potentials, 9.36 volts for zinc and 7.71 volts for copper (*2*).

LITERATURE CITED

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(2) Gould, E.S., "Inorganic Reactions and Structure," pp. 492–5, Holt, Rinehart & Winston, New York, 1962.

(3) Keely, W.M., Mathes, W.B., J. CHEM. ENG. DATA **10**, 231 (1965).

(4) Keely, W.M., Maynor, H.W., *Ibid.*, **9**, 170 (1964).

(5) Mellor, J.W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. **XI**, pp. 197-200, Longmans, Green, New York, 1931.

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

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CORRECTION

In the article "High Temperature *PVT* Properties of Sodium, Potassium, and Cesium" [J. CHEM. ENG. DATA **11**, 309 (1966)] in Table I, Experiment 17, the second temperature should be 2516.1 (not 2416.1); in Table II, Experiment 8, the 12th figure for specific volume should be 5.1371 (not 5.1293); in Table III, Experiment 35, the fourth temperature should be 2492.6 (not 2492.0) ~~and the~~ corresponding pressure should be 311.00 (not 211.00). The subcaption of Figure 6 should read: ■ Tepper; ● this work. In the first reference of Literature Cited the page number should be 315.

In the article "High Temperature Vapor Pressures of Sodium, Potassium, and Cesium" [J. CHEM. ENG. DATA **11**, 315 (1966)] on page 320, next to the last line in the second paragraph, first column, delete "with the contact." In reference 10 the volume number should be 11.

In the article "High Temperature Specific Volumes of Liquid Sodium, Potassium, and Cesium" [J. CHEM. ENG. DATA **11**, 320 (1966)] reference 9 should read: J. CHEM. ENG. DATA **11**, 309 (1966). Reference 10 should read: *Ibid.*, p. 315.

CORRECTION

In the article "Isobaric Vapor-Liquid Equilibrium of *n*-Heptane–*n*-Butanol System" [J. CHEM. ENG. DATA **11**, 147 (1966)], the following corrections should be made:

Equation 1 should be $\gamma_i = \frac{y_i P}{x_i p_i^0} \theta_i$

The caption for Figure 3 should read, α_1 *vs.* composition. Page 148, first column, line 13 should read, α_1, are calculated from experimental data with the help of. Page 148, second column, line 3 should read, measurement of temperature, $E(T)$; pressure, $E(P)$; and. Page 149, first column, line 21 should read, $D - J = 4.75 < 10$. Page 149, second column, line 10 should read, α_1 = dimensionless thermodynamic function in Equations 5 and 7.