Solid State Reaction Study of Hydrated and α-Aluminas With the Nitrates of Nickel and Cobalt

JOHN N. PATTISON[1], W. M. KEELY, and HARRY W. MAYNOR
Chemical Products Division, Chemetron Corp., Louisville, Ky.

HYDRATED and α-aluminas are widely applied as catalysts and catalyst carriers; therefore a better understanding is needed of the reactions and transformations that occur when mixtures of alumina and typical salts (nickel or cobalt nitrate hexahydrate) are calcined over wide temperature ranges. Jander and Grob (*3*) have heated mixtures of alpha alumina and nickel oxide in 1 to 1 molar ratio at various temperatures between 500° and 1100° C. No compound formation was reported below approximately 1000° C.; at this temperature crystals of a spinel became apparent, and at 1100° C. the lines of the original components practically disappeared. Milligan and Merten (*4*) concluded that nickel aluminate forms solid solution with each of the pure oxides. Natta and Passerini (*5*) discussed the formation of the spinel cobalt aluminate at 900° to 1000° C. Romeijn (*6*) reported cobalt aluminate as a normal spinel and nickel aluminate between the inverse and random spinel structure; whereas Greenwald, Pickart, and Grannis (*2*) described the nickel aluminate spinel as being almost completely inverted. The decomposition sequences of pure alumina hydrates have been studied in detail by Russell (*7*).

This report is concerned with the compound transformations that occur when a hydrated alumina (50% β-alumina trihydrate and 50% α-alumina monohydrate) mixed separately with the nitrates of nickel and cobalt is calcined at various temperatures ranging from 260° to 1200° C. A similar study was made substituting α-alumina for the hydrated alumina. Finally, the hydrated alumina was calcined independently and was compared with the alumina compounds observed in the calcined mixtures.

APPARATUS AND TECHNIQUE

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. Rotation is introduced to provide relative intensity measurements of higher accuracy and to reduce any possible orientation effects. In some cases where the sample exhibited extremely poor packing qualities the stationary sample holder was used.

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 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 and Girdler patterns: nickel oxide, α-alumina monohydrate, β-alumina trihydrate, γ-alumina, θ-alumina, α-alumina and cobalt aluminate (*1*); nickel aluminate (Girdler pattern obtained by calcining 1 to 1 molar mixture of hydrated alumina and nickel nitrate hexahydrate for 20 hours at 1320° C.) and cobalto-cobaltic oxide (Girdler pattern obtained by calcining cobalt nitrate hexahydrate 16 hours at 650° C.).

PREPARATION OF MATERIALS

Chemicals. Nickel nitrate hexahydrate, analytical reagent, Mallinckrodt Chemical Co.

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

Hydrated alumina (approximately 50% β-alumina trihydrate and 50% α-alumina monohydrate, Filtrol Corp., confirmed by weight loss and x-ray diffraction pattern. The alumina contained trace amounts of calcium, magnesium, sulfur, silicon, sodium and iron.

α-Alumina, prepared by calcining Filtrol hydrated alumina for 24 hours at 1260° C., and confirmed by x-ray diffraction pattern.

Procedure. One mole of hydrated nitrate (nickel nitrate hexahydrate and cobalt nitrate hexahydrate used separately) is mixed with 1 mole of alumina (hydrated alumina and α-alumina used separately) 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 for 16 to 20 hours at temperatures ranging from 260° to 1200° C.

DISCUSSION

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

There is a greater tendency for the nickel aluminate to form using the hydrated alumina than with α-alumina. Calcinations at 260° C. for shorter periods results in small amounts of β-alumina trihydrate and incompletely decomposed nickel compounds. The cobalt series shows a similar trend in alumina transformation and aluminate formation.

Cobalt aluminate is present in slightly greater amounts than nickel aluminate at corresponding temperatures. The cobalt study shows small amounts of β-alumina trihydrate at 260° C. whereas the nickel study does not, but this

---

[1] Present address, Rock Hill Laboratory, Chemical Products Division, Chemetron Corp., Newport, Tenn.

difference is not considered significant because the calcination conditions are borderline for complete trihydrate decomposition. The aluminate starts to form at 870° C. but the original products are still present at 1200° C. This disagrees in detail with the work of Jander and Grob (*3*).

Table I. Calcination Products of the 1 to 1 Molar Mixture of Hydrated Nitrates with α-Alumina and with Hydrated Alumina

(50% β- Alumina Trihydrate and 50% α-Alumina Monohydrate)

Time, Hours	Temp., ° C.	Compounds Identified $Ni(NO_3)_2 \cdot 6H_2O$-hydrated alumina	 $Ni(NO_3)_2 \cdot 6H_2O$-α-alumina
16–18	260	NiO α-$Al_2O_3 \cdot H_2O$	NiO α-Al_2O_3
16–18	480	NiO γ-Al_2O_3	NiO α-Al_2O_3
18	650	NiO γ-Al_2O_3	
16–18	870	NiO $NiAl_2O_4$ γ-Al_2O_3	NiO α-Al_2O_3
16–18	1200	$NiAl_2O_4$ NiO α-Al_2O_3	NiO $NiAl_2O_4$ α-Al_2O_3
		$Co(NO_3)_2 \cdot 6H_2O$-hydrated alumina	$Co(NO_3)_2 \cdot 6H_2O$-α-alumina
16–20	260	CO_3O_4	CO_3O_4
16–20	260	Co_3O_4 α-$Al_2O_3 \cdot H_2O$ β-$Al_2O_3 \cdot 3H_2O$	Co_3O_4 α-Al_2O_3
16–20	480	Co_3O_4 γ-Al_2O_3	Co_3O_4 α-Al_2O_3
16	650	Co_3O_4 γ-Al_2O_3	
16–20	870	Co_3O_4 $CoAl_2O_4$ γ-Al_2O_3	Co_3O_4 α-Al_2O_3
16–19	1200	$CoAl_2O_4$ Co_3O_4 α-Al_2O_3	Co_3O_4 $CoAl_2O_4$ α-Al_2O_3

The α-alumina peaks are much smaller than expected in both the nickel nitrate hexahydrate–α-alumina and the cobalt nitrate hexahydrate–α-alumina studies. Crystalline α-alumina is present in a highly attenuated state.

A similar series of calcinations for unmixed hydrated alumina is presented in Table II.

Table II. Calcination Products of 50% β-Alumina Trihydrate and 50% α-Alumina Monohydrate

Time, Hr.	Temp., ° C.	Compd. Identified
16	260	α-$Al_2O_3 \cdot H_2O$ β-$Al_2O_3 \cdot 3H_2O$
16	480	γ-Al_2O_3
19½	650	γ-Al_2O_3
19	870	γ-Al_2O_3 θ-Al_2O_3
8	1200	α-Al_2O_3

There is no positive evidence for γ-alumina at 260° C.; whereas Russell (*7*) indicates its formation at 250° C. Purity and particle size could account for this difference. Hydrated alumina alone shows approximately the same transformation series as was observed for the nickel and cobalt mixtures with the exception of θ-alumina appearing at 870° C.

LITERATURE CITED

(1) Am. Soc. Testing Materials, X-Ray Powder Data Cards, 1-0307, 1-1303, 3-0896, 4-0835, 4-0876, 5-0190, and 5-0712.

(2) Greenwald, S., Pickart, S.J., Grannis, F.H., *J. Chem. Phys.* **22**, 1597–1600 (1954).

(3) Jander, W., Grob, K., *Z. anorg. Chem.* **245**, 67–84 (1940).

(4) Milligan, W.O., Merten, L., *J. Phys. Chem.* **50**, 465–70 (1946).

(5) Natta, G., Passerini, L., *Gazz. chim. ital.* **59**, 280–8 (1929).

(6) Romeijn, F.C., (N.V. Phillips Gloeilampenfabrieken, Eindhoven, Netherlands), *Philips Research Repts.* **8**, 321–42 (1953).

(7) Russell, A.B., others, Alcoa Research Lab. Tech. Paper No. **10** (Revised) 1956.

RECEIVED for review January 25, 1960. Accepted June 6, 1960.