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Preparation of Niobates of Rhodium and Nickel by Chemical Mixing Methods

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Synopsis. Niobates of rhodium or nickel were prepared by double decomposition of aqueous rhodium or nickel salt solution with tetraalkylammonium polyniobate and with alkali orthoniobate or metaniobate, as well as by decomposition of mixed citrates of niobium with Rh or Ni. The niobates thus prepared were shown by X-ray diffraction to be well-crystallized and essentially monophasic. The calcination temperature required to achieve crystallization of all the samples is much lower than ceramic methods.

Double oxides, owing to their outstanding physicochemical properties in many aspects (catalysts, superconductors, electro-optics, magnetic materials), are becoming ever more important high-technique materials. In ceramic methods, formerly being the most popular route of preparation, very high temperature of calcination is usually needed to attain complete solid phase reaction. Consequently, a double oxide of very low surface area, and with more important, of rather low homogeneity, resulted in, even though repeated calcination crushing-pelleting cycles were applied. Recently, to prepare mixed/double oxide with two or more cations, by chemical mixing methods to achieve most intimate mixing and high homogeneity, has been receiving more and more attention.[1]

One of the methods most widely applied to the synthesis of double oxides is the thermal decomposition of mixed metal citrates, as was first proposed by Courtry et al.[2,3] However, no attempts have been tried to use the citrate complexation method for the synthesis of double oxides comprising of niobates. And there seems no preparation of related double oxides containing the metals of noble metal (Rh etc.) by this method ever published. Some publications of Soviet scientists mentioned the precipitation of niobates of divalent and trivalent base metal cations, using potassium metaniobate or orthoniobate.[4–6] Moreover, Spinner and his colleagues[7,8] have studied a new family of isopolyanions of niobium(V), prepared by reacting niobia with tetraalkylammonium hydroxide. Nevertheless, no paper has ever been published as yet on the formation of rhodium(III) niobates.

In spite of the scarce knowledge about the citrate of niobium and rhodium and the solution chemistry of isopolyniobates, attempts to prepare niobates of rhodium(III) and nickel(II) via these chemical mixing methods, using citrate, metaniobate, orthoniobate, and tetraalkylammonium, were tried, and the results were described in this paper.

Experimental

Preparation via Tetraalkylammonium Polyniobate. Tetra-*n*-propylammonium polyniobate was prepared at first by dissolving hydrous niobic acid, freshly precipitated from aqueous solution of $(NH_4)_3[NbO(C_2O_4)_3]$ with ammoina water, in $[N(n\text{-}C_3H_7)_4]OH$. $RhCl_3$ was dissolved in small amount of water and stirred vigorously. Immediately after adding small amount of ammonia water to make the rhodium solution slightly basic, calculated amount of tetrapropylammonium isopolyniobate solution was added to it to make the atomic ratio of Nb to Rh=1.0. The golden yellow precipitate, designated as RNA, was filtered, washed thoroughly, and dried.

When nickel(II) acetate was used instead of $RhCl_3$, with Nb/Ni atomic ratio=2, a pale blue precipitate was obtained in a similar manner, and was designated as NNA.

Preparation via Potassium Metaniobate or Orthoniobate. Concentrated aqueous solutions of potassium metaniobate and orthoniobate were prepared according to Windmaisser.[9] Calculated amount of potassium metaniobate solution was diluted appropriately, and then mixed under vigorous stirring with stoichiometric amount of ammoniacal nickel(II) acetate (at Nb/Ni=2) solution. After filtration, through washing, and drying, a pale blue precipitate was obtained and designated as NNB-1. Another Ni–Nb complex (NNB-2) was prepared in a similar manner, except that potassium orthoniobate solution was used.

For preparing rhodium niobate, $Rh(NO_3)_3$ and potassium orthoniobate solutions were used at Nb/Rh atomic ratio=1. A golden brown solid was obtained after filtration, through washing, and drying, and was designated as RNB.

Preparation via Mixed Metal Citrate Solutions. Aqueous solution of rhodium(III) citrate was prepared through the reaction of $RhCl_3$, fresh silver hydroxide, and citric acid. The silver hydroxide was used to exclude the presence of chloride ion. Niobium citrate solution was prepared by dissolving hydrous niobic acid in a 2 M (1 M=1 mol dm^{-3}) citric acid. Then, calculated amounts of the aqueous citrate solutions of niobium and rhodium, with Nb/Rh=1.0, were mixed in a separable flask without further dilution. A cover connected to a condenser and suction flask was fixed onto the flask, seated with viton O-ring, and fastened with a metallic clamp. The system was stirred magnetically, evacuated with water jet aspirator, and heated with a heating stripe to evaporate off the water at 323-333 K under a residual pressure of about 140-160 Torr. The thoroughly dried solid appeared as a vitreous glassy residue, designated as RNC, and was easily taken out from the separable flask after dismantling the cover.

The citrate solution of nickel and niobium (NNC), with Nb/Ni=2, was prepared in a similar manner, using nickel(II) acetate instead of $RhCl_3$.

XRD patterns of the above-mentioned complex oxides, after calcined at a high temperature, were obtained with an X-ray diffractometer (Rigaku Co., Ltd.) equipped with a graphite monochromator for CuK_α (40 kV, 30 mA) radiation.[10]

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Results and Discussion

The XRD patterns for the double oxides of Ni and Nb, prepared by using tetrapropylammonium hydroxide (NNA) and calcined at 873 and 1023 K were shown in Fig. 1. For the sample NNA calcined at 1023 K, the whole set of X-ray diffraction peaks, as registered in JCPDS, are manifested, and substantiates an essentially monophasic columbite $NiNb_2O_6$ structure. However, for the sample calcined at 873 K, not all the peaks related to the columbite $NiNb_2O_6$ are manifested; especially the sharp peaks at d=3.61 and 2.93 Å, corresponding to the diffractions from (130) and (131) planes respectively, seems to be inundated in a broad peak. Instead, two medium peaks (d=2.50 and 1.706 Å), corresponding to the diffractions from (002) and (062) planes become the strongest ones. This implies the preferential growth in some orientations of the columbite crystal at lower temperature, and late maturing in some other orientations at higher temperatures.

For the double oxide of Ni and Nb, prepared by double decomposition with potassium metaniobate (NNB-1), the sample calcined at 1023 K shows a diffraction pattern of pure $NiNb_2O_6$ columbite, as shown in Fig. 2(1). However, in the sample prepared by using potassium orthoniobate (NNB-2), a considerable amount of nickel oxide (NiO) was present (see Fig. 2(2)). The NNC preparation, after a calcination at 1023 K, shows a nice conformity with standard XRD pattern of $NiNb_2O_6$ columbite, as is demonstrated in Fig. 2(3).

Wichmann et al.[11-13] showed that various modifications of nickel niobate (e.g., columbite and rutile form of $NiNb_2O_6$, as well as I- and II-form of $Ni_4Nb_2O_9$) formed by means of solid phase reaction of nickel oxide or oxalate with niobia only after a calcination from 1523 to 1723 K. Obviously, the formation of nickel niobate as crystalline columbite can be achieved by the present methods at much lower temperature.

The XRD patterns of the complex oxide of Rh and Nb, prepared by the three different methods and calcined at 1023 K, are shown in Fig. 3. The complex oxide prepared by tetraalkylammonium complexation method (RNA) is demonstrated to be consisted essentially of rhodium niobate phase, with only very small amount of Rh_2O_3. For the sample prepared by the citrate method (RNC), essentially monophasic $RhNbO_4$ is obtained together with very small amount of unidentified phase. Meanwhile, the RNB sample, prepared by double decomposition with potassium orthoniobate, is shown to possess highest purity of monophasic $RhNbO_4$; only trace amount of T-Nb_2O_5 is present. It should be noted that the XRD patterns of the three samples in Fig. 3 are in reasonable agreement with the Rietveld refinement patterns of the $RhNbO_4$ compound prepared on a SiO_2 support.[10]

So far as the authors aware, no publication has been observed for the synthesis of noble metal niobates by chemical mixing methods. Rhodium niobate was prepared by Shaplygin et al.[14] via calcining rhodium oxide and niobium oxide at 1273 K. Silica-supported rhodium niobate catalysts have been successfully prepared by the present authors as monophasic solids

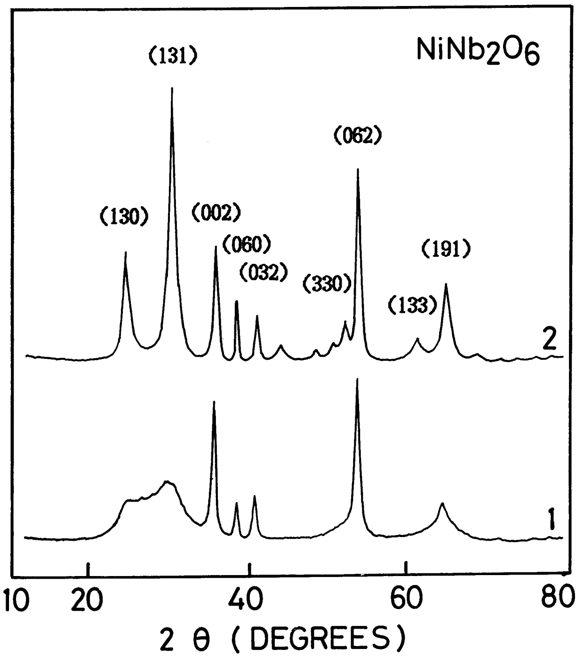

Fig. 1. X-Ray diffraction patterns of the Ni–Nb complex oxide (NNA) after calcination (1) at 873 K and (2) at 1023 K.

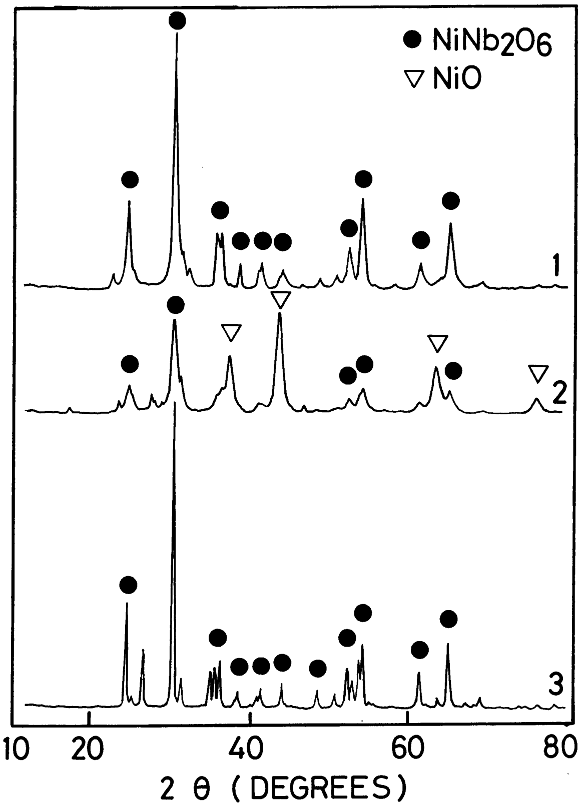

Fig. 2. X-Ray diffraction patterns of the Ni–Nb complex oxide after calcination at 1023 K: (1) NNB-1, (2) NNB-2, (3) NNC.

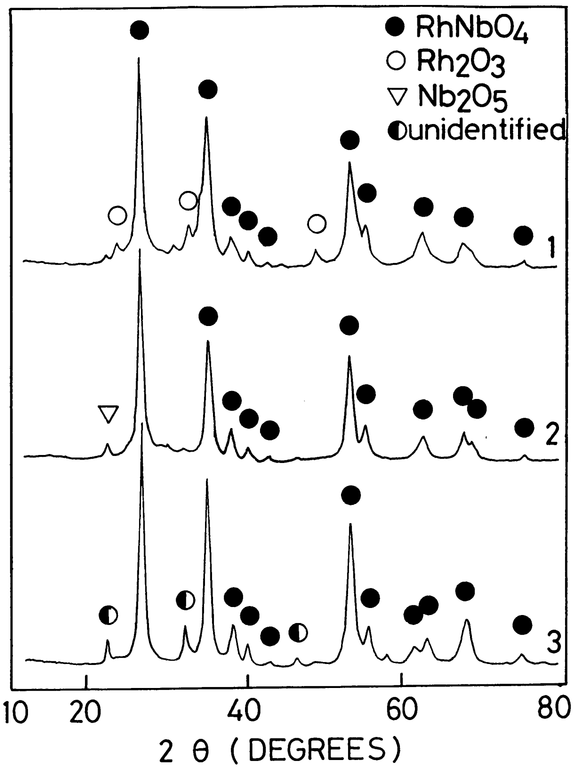

Fig. 3. X-Ray diffraction patterns of the Rh–Nb complex oxide after calcination at 1023 K: (1) RNA, (2) RNB, (3) RNC.

also and have been studied for the strong metal-oxide (Rh-niobia) interaction after the decomposition of $RhNbO_4$ by H_2 reduction.[15] No other rhodium niobates of different stoichiometries were known. There is also very few information about the chemistry of rhodium niobate. The present results together with those reported in Ref. 15 showed that the preparation of rhodium niobates, either unsupported or silica-supported, as a pure phase can be accomplished by either of the three new chemical mixing methods.

In order to prepare monophasic niobate of nickel and rhodium by means of double decomposition with alkali niobates, potassium metaniobate and orthoniobate solutions should be used for nickel niobate and rhodium niobate, respectively. In practice, the NNB-1 and RNB samples were prepared by observing this point. Tanirbergenov et al.[5] showed that nickel orthoniobate can be prepared by double decomposition of nickel salt with potassium orthoniobate. But the nickel orthoniobate thus prepared underwent decomposition to nickel metaniobate and nickel oxide (NiO) if it was calcined to 973 K. This may be the case in the sample NNB-2. On the other hand, Sych et al.[6] suggested that the metaniobates of trivalent cation, such as Bi(III) and Cr(III), are liable to be decomposed to corresponding orthoniobates with liberation of niobia after calcination. Actually, the precipitate obtained in this laboratory from double decomposition of $Rh(NO_3)_3$ and potassium metaniobate gives a multiphasic solid, containing considerable amount of T-Nb_2O_5, after calcination to 1023 K.

Among the three chemical mixing methods for the preparation of nickel niobate, the citric method (NNC) may be more preferable than the other two methods, as could be seen by comparing the XRD patterns of sample NNA, NNB-1, and NNC. The sample NNA is preferentially oriented. The sample NNB-1, although much better than NNB-2 in crystallographic sense, as is prepared from a solution containing alkali metal ion, might not be exempt from its contamination.

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