Journal of Alloys and Compounds, 182 (1992) 189–193
JALCOM 142

Preparation of manganous(II) tungstate by a precipitation method

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(Received September 25, 1991)

Abstract

The conditions of preparation of stoichiometric $MnWO_4$ by a precipitation method have been investigated. The composition of the solid phases obtained under different conditions is investigated by X-ray, thermal, IR and atomic absorption spectral analyses. On the basis of the pH and concentration dependences of the precipitate compositions it is established that, irrespective of the initial solution concentrations, stoichiometric $MnWO_4$ with a W:Mn atomic ratio of 1.0 is formed during precipitation in the alkaline region. The excess of Mn^{2+} and $WO_4{}^{2-}$ does not affect the precipitate compositions. A complex mixture of polytungstate ions is obtained in acid media (pH below 7.5), and the further decrease of the pH value is accompanied by an increase of the contribution of the polytungstate ions having a higher tungsten content. The drop in the W:Mn ratio of precipitates obtained in the strongly acid region can be attributed to the higher solubility of the polymeric ions under these conditions.

1. Introduction

During recent years, interest in metal tungstates has increased. This is attributed to the fact that a large number of them possess valuable properties and are promising as new materials for modern technologies. A series of tungstates are already widely applied to the preparation of single crystals for laser applications; others are superconducting and have good emission characteristics allowing their use in modern electronics [1, 2]. The tungstates of divalent metals, some of which are utilized as industrial luminophores [3], are of special interest.

The preparation of divalent metal tungstates in a thermal way is described in a large number of publications [4–7]. Oxides or easily decomposing salts and tungsten trioxides are usually applied. The process takes place to completion at about and above 1000 °C. The data on the preparation of tungstates by precipitation are scarce. This is explained by the difficulties associated with the precipitation compounds of a stoichiometric composition. It is known that the composition of the precipitates depends strongly on

0925-8388/92/$5.00

the state of tungsten ions during precipitation [8, 9]. It is also known that in the aqueous solutions of the tungstates used polycondensation processes occur which lead to complex equilibria between different isopoly tungstate ions. The kinds of ions and the quantitative ratios between them depend on a number of factors such as pH value, temperature, W(VI) concentration etc. [3, 10].

Karagjozova [11, 12] has investigated thoroughly the polymerization of Mo(VI) in concentrated paramolybdate solutions and has assumed the existence of homologous series of polymolybdate ions.

The presence of a similar homologous series in the case of polytungstate ions is also supposed.

The purpose of the present work is to study the polymerization of W(VI) in aqueous solutions with a concentration of 0.1–0.4 M and to estimate the possibility of obtaining Me(II) tungstates by precipitation. The equilibrium between different forms of polytungstate ions is studied on the basis of the Mn(II)–W(VI)–H_2O system.

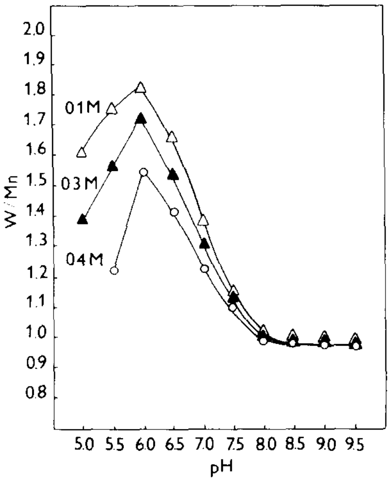
2. Experimental details

Precipitation was achieved by slow addition with continuous stirring of aqueous solutions of manganous(II) nitrate to sodium tungstate heated to 60 °C. The pH of the initial solutions was maintained constant during the precipitation process by addition of 10% NH_3 solution or 10% HNO_3. The composition of the precipitates obtained was investigated by X-ray, thermal, IR spectroscopic and atomic absorption analysis.

3. Results and discussion

Figure 1 presents the dependence of the compositions of the precipitates (in terms of the W:Mn atomic ratio) on the pH value during the precipitation.

Obviously, irrespective of the concentration of the initial solutions, the W:Mn atomic ratio in the precipitate obtained is 1.0 when precipitation takes place in the alkali region (ph = 7.5); *i.e.* a light green, dense, well-filtered precipitate of stoichiometric $MnWO_4$ is formed in all cases. The investigations show that the excess of Mn(II) and WO_4^{2-} ions does not affect the precipitate compositions. The data from analysis of the solid phases obtained at lower pH values during the precipitation evidence the occurrence of much more complicated processes. The W:Mn atomic ratio rapidly increases and passes through a maximum at about pH = 6.0. Simultaneously, the amount of the precipitate obtained essentially decreases. Similar results were also obtained by Pitzjuga *et al.* [13] after mixing aqueous solutions of $MnCl_2$ and Na_2WO_4 without correction of pH. When the pH value during the precipitation is below 5.5, the colour of the precipitate changes, and at pH below 5.0 the precipitate is single phase and contains pure tungstic acid.



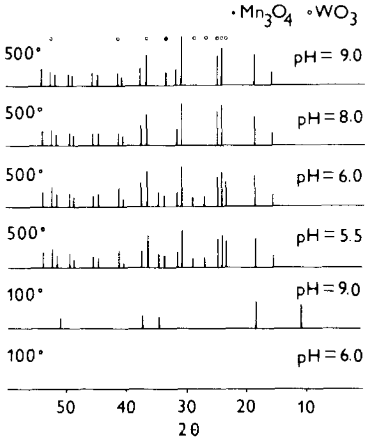


Fig. 1. Dependence of the compositions of the precipitates on the pH value: △, 0.1 M; ▲, 0.3 M; ○, 0.4 M.

Fig. 2. Diffraction patterns of samples obtained under different conditions (●, Mn_3O_4; ○, WO_3): top, 500 °C, pH = 9.0; second, 500 °C, pH = 8.0; third, 500 °C, pH = 6.0; fourth, 500 °C, pH = 5.5; fifth, 100 °C, pH = 9.0; bottom, 100 °C, pH = 6.0.

According to Karagjozova [12], in the paramolybdate solution there is a homologous series of polymolybdate ions which are dependent on pH. This suggestion has been confirmed by our studies on the Mn(II)–MoO_4^{2-}–H_2O system. Precipitates with the following stoichiometric composition were isolated and characterized: $MnMoO_{4.1}\cdot 5H_2O$, $Mn_3Mo_3O_{12}\cdot H_2O$ and $Mn_3Mo_4O_{15}\cdot H_2O$ [14]. However, all efforts to obtain tungstates with an analogous composition have failed. Evidently, much more complicated equilibria between the polytungstate ions are present in this case and it is difficult to establish the boundaries of their existence.

Our investigations have shown that in the alkaline region there are tungstate ions with the composition WO_4^{2-}. With rising concentration the boundary of their existence is shifted towards higher pH values. In the acid region there is a complex mixture of polytungstate ions with a higher tungsten concentration. The decrease in W:Mn ratio of the precipitates obtained in the strongly acidic medium can be ascribed to the higher solubility of polymeric ions under these conditions. An analogous effect has been observed with molybdate ions [14].

The above conclusions were confirmed by X-ray, IR spectroscopy and thermal analyses. Figure 2 presents results from X-ray studies of samples obtained under different conditions, dried at 100 °C, and then calcined for 4 h at 500 °C.

It is obvious that the precipitates obtained in acid medium and dried at 100 °C are amorphous. The samples precipitated in the alkali region are relatively well-crystallized phases. The thermal treatment of the samples leads to the formations of well-shaped crystals of stoichiometric $MnWO_4$ (ph = 8.0) or of a mixture of $MnWO_4$ and WO_3 (ph = 5.5 and 6.0). The presence of Mn_3O_4 in the sample obtained at pH = 9.0 can be attributed to the coprecipitation of certain amounts of $Mn(OH)_2$ under these conditions. The results from X-ray analysis are confirmed by the IR spectra shown in Fig. 3. Comparison of these spectra leads to the conclusions that the precipitates obtained differ in composition and contain no free initial substances.

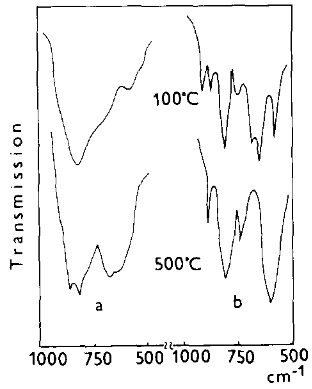
The sample precipitated at pH = 8.0 is characterized by distinct bands at 504, 574, 651, 681, 725, 808, 874 and 915 cm^{-2}. The intensity of these bands abruptly drops with rising temperature due to the formation of a new phase. This process is accompanied by a visible shift of the height and position of the absorption bands within the 700–1000 cm^{-1} region, which is demonstrated by the spectrum of the sample calcined at 500 °C.

It should be pointed out that there are bands at 591, 731, 801 and 882 cm^{-1} which are specific to pure $MnWO_4$ only and are described in detail by other authors.

The results on the sample precipitated at pH = 6.0 and dried successively at 100 °C for 6 h and at 500 °C for 4 h are quite different. In both cases the IR spectra are characterized by the absence of distinct absorption bands. This confirms the conclusion that under these conditions the dried samples contain a complex mixture of polytungstates, while the samples calcined at 500 °C contain a mixture of $MnWO_4$ and WO_3.

Figure 4 shows the results from differential thermal analysis (DTA) of the samples obtained by precipitation at pH = 8.0 and 6.0.

The DTA curve of the former sample is characterized by an endothermic effect at 225 °C followed by a broad indistinct exothermic effect. The former effect is a result of the dehydration of crystallohydrate formed during the precipitation, while the latter effect is associated with crystallization of $MnWO_4$.



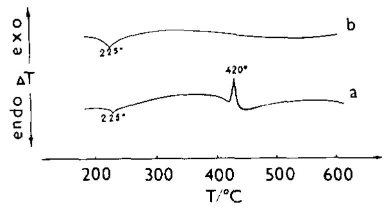


Fig. 3. IR spectra of samples precipitated at pH = 6 (curves a) and pH = 8 (curves b): upper curves, 100 °C; lower curves, 500 °C.

Fig. 4. DTA curves of the samples obtained by precipitation at pH = 6 (curve a) and pH = 8 (curve b).

The TG curve of the sample shows that the crystal water is 8.3% of the whole weight. This allows the suggestion that the composition of the precipitate obtained is close to $MnWO_4 \cdot 1.4H_2O$.

The DTA curve of the second sample exhibits a broad indistinct exothermic peak followed by a pronounced exothermic effect at 420 °C. The former can be attributed to decomposition of polytungstates and crystallization of $MnWO_4$, while the latter may be associated with crystallization of WO_3 formed in an excessive amount under these conditions.

The results obtained lead to the conclusion that the composition of the precipitates depends strongly on the precipitation conditions and the concentration of the solutions used. Pure $MnWO_4$ can be obtained in the alkaline region only, where there are simple WO_4^{2-} ions. The precipitates formed in the acid region contain a complex mixture of polytungstates, whereas a precipitate of tungstic acid is observed below $pH = 5.0$.

Additional investigations have shown that the conclusions about the $Mn(II)–WO_4^{2-}–H_2O$ system ar also valid for the preparation of tungstates of other divalent metals, such as zinc, nickel, cobalt and calcium [15]. However, these conclusions cannot be applied to the systems $Me^{3+}–WO_4–H_2O$ where the appearance of tungstates of the type $NaMe(WO_4)_2$ and Me_2WO_6 is possible.

References

1 K. Nassau, J. W. Shiever and E. T. Keve, *J. Solid State Chem.*, *3* (1971) 411.

2 K. Nassau, H. J. Levinstein and G. M. Loiacono, *J. Phys. Chem. Solids*, *26* (1965) 1808.

3 M. V. Mohosoev, *Himija Soedinenii Mo(VI) i W(VI)*, Nauka, Moscow, 1979.

4 V. K. Trunov and L. M. Kovba, *Neorg. Mater.*, *1* (1966) 151.

5 D. W. Langebeck, H. Pobloth and H. Reif, *DDR Patentschrift 15 576*, 4 October 1958.

6 J. D. Kozmanov, *Zh. Fiz. Khim.*, *8* (1957) 1861.

7 L. G. Van Uitert, J. J. Rubin and W. A. Bonner, *J. Am. Ceram. Soc.*, *46* (1963) 10.

8 D. L. Kepert, *Prog. Inorg. Chem.*, *4* (1962) 199.

9 U. Stollenwerk, *Prax. Naturwiss.*, *Teil 3*, *45* (1977) 31.

10 O. Glemser, W. Holznagel and W. Holtje, *Z. Naturforsch.*, *206* (1965) 725.

11 S. M. Karagjozova, *CR Acad. Bulg. Sci.*, *11* (1982) 1487.

12 S. M. Karagjozova, *Mater. Res. Bull.*, *20* (1985) 601.

13 V. N. Pitzjuga, M. V. Mohosoev and M. N. Pitzjuga, *Himija i Tehnologija Mo i W*, Vol. 2, 1974, p. 108.

14 K. Ivanov, P. Litcheva, D. Klissurski and T. Popov, *Bulgarian Patent 47 214*, 1989.

15 St. Krustev, *Dissertation*, Agrarian University, Plovdiv, 1991.