3448 *Inorg. Chem.* **1998,** *37,* 3448−3449

Synthesis of Reduced Transition-Metal Oxides with Hydroxylamine Hydrochloride

V. Manivannan and J. B. Goodenough*

Center for Materials Science and Engineering, ETC 9.102, The University of Texas at Austin, Austin, Texas 78712

Received March 12, 1998

Introduction

The realization of technologically important materials commonly requires access to metastable structures, low-temperature phases, or stable phases in the form of fine particles. This requirement has led to an extensive interest in low-temperature synthetic techniques such as sol−gel processing,[1] molecular precursors,[2] chemical intercalation/deintercalation,[3] molten flux methods,[4] and ion exchange.[5] We present here a novel approach to obtain reduced transition-metal oxides in aqueous solution that uses hydroxylamine hydrochloride as a reducing agent. Hydroxylamine hydrochloride is used extensively in organic chemical synthesis. For example, reaction of spironaphthalenes with hydroxylamine hydrochloride produces heterocyclic compounds such as naphthisoxazoles.[6] Synthesis using hydroxylamine hydrochloride in the presence of PVP (polyvinyl pyrrolidone) at 277 K gives unsintered Pt particles of mean diameter ≈2 nm. The reducing power of the solution has been increased by adding glucose, as in synthesis of phosphovanadic acid, which is used as a catalyst for the production of maleic anhydride.[7] In a preliminary report we have shown that hydroxylamine hydrochloride can be used to obtain rutile vanadium oxides in aqueous solution.[8] Here we explore the range of reduced oxides that can be accessed by this reducing agent by using it to obtain reduced binary oxides of chromium, iron, molybdenum, and tungsten.

Experimental Section

Vanadates, chromates, molybdates, and tungstate form $(MO_4)^{n-}$ (M = V, Cr, Mo, W) oxoions in aqueous solutions. These oxoions transform to complex polyions on varying the pH of the medium and condense to form binary oxides VO_2, Cr_2O_3, MoO_2, or WO_2. Addition of aqueous hydroxylamine hydrochloride to aqueous solutions of ammonium metal vanadates, chromates, molybdates, or tungstates at a desired pH, depending on the reaction and end-product (see Table 1), results in an instantaneous color change due to the reduction of the transition-metal ions. Continued slow addition of hydroxylamine hydrochloride from a buret at a given pH, maintained by adding HCl drops, results in deep-colored gels. The dark precipitate/gel was allowed to settle overnight, filtered, washed with water, dried, and stored in a desiccator. The byproduct of the reaction between hydroxylamine hydrochloride and ammonium metalate is NH_4Cl, which is soluble in water. The nature of the phase formed depends strongly on the concentration of the solution and the volume of the solution in addition to the pH of the medium. Through a series of experiments, we have identified the conditions to obtain different binary oxides; the final phases formed are summarized in Table 1.

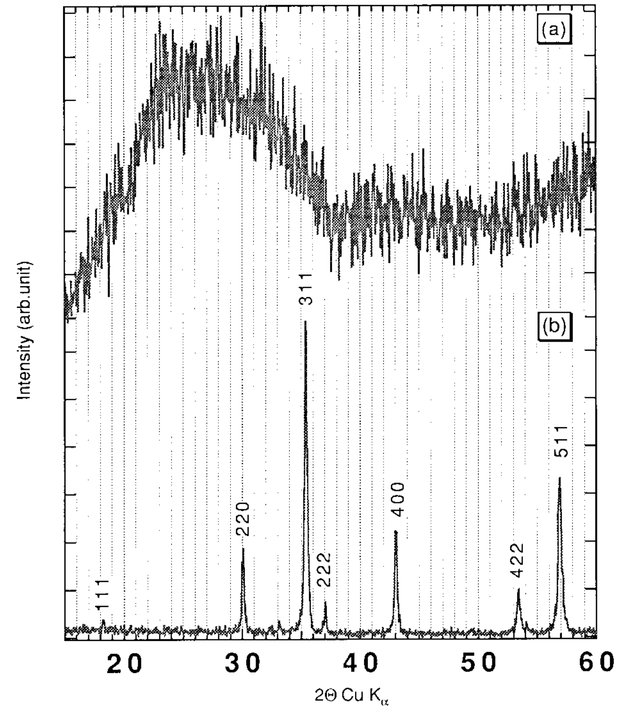

Figure 1. X-ray powder diffraction patterns of the reduced iron oxide (a) as-prepared gel and (b) after heating the gel in N_2 atmosphere in DSC up to 450 °C at a heating rate of 10 °C/min.

The as-prepared products are amorphous in nature as indicated by the absence of any X-ray diffraction (XRD) Bragg reflections in the 2θ range 10−60°. These products crystallize at 300−500 °C in an inert atmosphere to yield the binary oxide products. For example, reduction of 0.25 M solution of ferric ammonium chloride with 2.5 M solution of hydroxylamine hydrochloride at pH 5 gave a product with the amorphous XRD pattern of Figure 1a. Differential scanning calorimetry (DSC) of the as-prepared sample recorded in flowing N_2 atmosphere with a Perkin-Elmer Series 7 Thermal Analysis System is shown in Figure 2. The sharp endothermic/exothermic events just below and above 300 °C correspond to the loss of H_2O followed by the crystallization of Fe_3O_4. The XRD of the crystallized product is shown in Figure 1b; it shows the formation of single-phase Fe_3O_4 without any trace of impurity. Figure 3 shows the XRD patterns for the other products listed in Table 1.

Single-phase products without any impurity are also formed for binary Cr, Mo, and V oxides. The as-prepared sample obtained from ammonium molybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ with 0.1 M hydroxylamine hydrochloride, on heating in an inert atmosphere, showed a moderate exotherm at 425 °C. To improve the crystallinity of the product, the

---

* Corresponding author.

(1) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, 259−341.

(2) Longo, J. M.; Horowitz, H. S. In *Preparation and Characterization of Materials*; Honig, J. M., Rao, C. N. R., Eds.; Academic Press: New York, 1981; pp 29−46.

(3) Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry;* Academic Press: New York, 1982.

(4) Ham, W. K.; Holland, G. F.; Stacy, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 5214−5215.

(5) England, W. A.; Goodenough, J. B.; Wiseman, P. J. *J. Solid State Chem.* **1983**, *49*, 289−299.

(6) Kasturi, T. R.; Sattigeri, P. V.; Pragnacharyulu, P. V.; Cameroon, T. S.; Pradeep, B. *Tetrahedron* **1995**, *51*, 3051−3060.

(7) Kodama, K. *Jpn. Kokai Tokkyo Koho* **1981**, *81*, 14−17.

(8) Manivannan, V.; Goodenough, J. B. *Mater. Res. Bull.* **1998** (in press).

S0020-1669(98)00275-4 CCC: $15.00

Table 1. Reduced Transition-Metal Oxides Obtained by Hydroxylamine Reduction

metalate		hydroxylamine				
concn (M)	vol (mL)	concn (M)	vol (mL)	pH	cryst temp (°C)	final products
0.25 $(NH_4)_3Fe(C_2O_4)_3{\cdot}3H_2O$	100	2.5 $NH_2OH{\cdot}HCl$	100	6	300	Fe_3O_4
0.01 $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$	100	2.5 $NH_2OH{\cdot}HCl$	100	5	300	$(NH_4)_{0.33}WO_3$
0.25 $(NH_4)_2Cr_2O_7$	100	2.5 $NH_2OH{\cdot}HCl$	75	5	500	Cr_2O_3
0.25 $2NH_4Cl{\cdot}FeCl_3{\cdot}H_2O$	100	2.5 $NH_2OH{\cdot}HCl$	100	5	275	Fe_3O_4
0.1 $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	75	0.1 $NH_2OH{\cdot}HCl$	75	7	425	MoO_2[a]
0.25 NH_4VO_3	100	0.25 $NH_2OH{\cdot}HCl$	100	5	475	VO_2

[a] After annealing for 24 h in an evacuated tube.

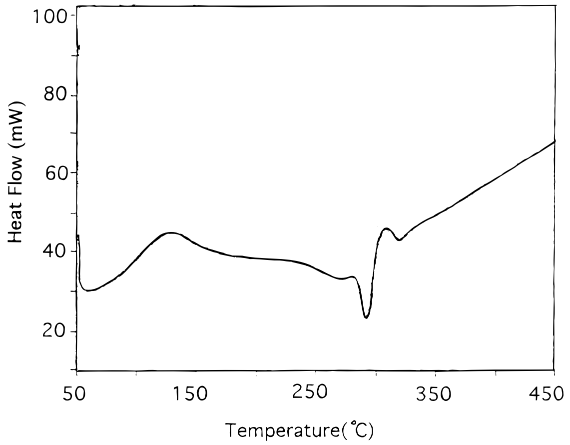

Figure 2. DSC curve of the amorphous Fe_3O_4 recorded in N_2 atmosphere with a heating rate of 10 °C/min and a sample weight of 15 mg.

sample was sealed in an evacuated quartz tube, heated in a furnace at 600 °C for 24 h, and slowly cooled. The resulting product is single-phase MoO_2. Well-crystallized Cr_2O_3 is obtained when ammonium dichromate, $(NH_4)_2Cr_2O_7$, is reduced with hydroxylamine hydrochloride solution. In the case of ammonium paratungstate, the resulting product is $(NH_4)_{0.33}WO_3$. We believe the reducing power at pH 5 is not sufficient to reduce ammonium paratungstate directly to WO_2.

Conclusion

Hydroxylamine hydrochloride has been used as a reducing agent to obtain fine particle binary metal oxides from their respective ammonium salts. Exploration of this technique in the presence of other cations may lead to the formation of ternary oxides in solution. The method described in this communication should be applicable to the synthesis of metastable or low-temperature phases with interesting physical and structural properties.

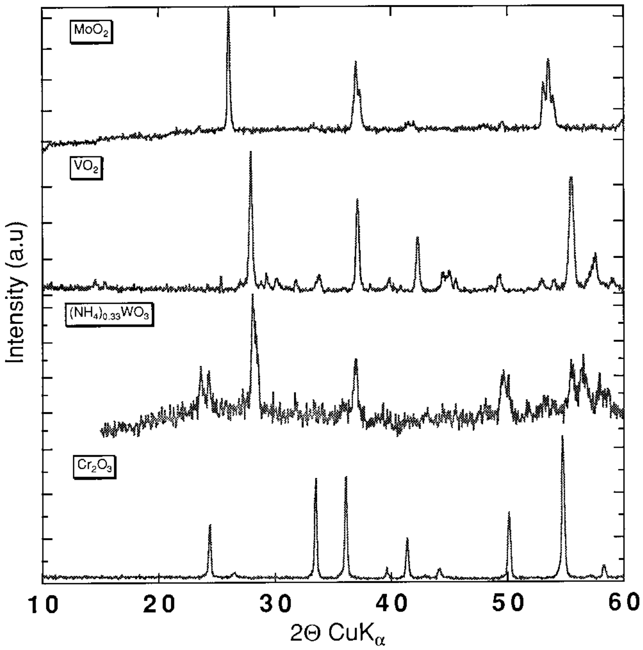

Figure 3. XRD patterns of the reduced binary oxide products listed in Table 1.

Acknowledgment. Financial support from Robert Welch Foundation, Houston, Texas is gratefully acknowledged for the support of this research.

IC9802754