J. Am. Chem. Soc. **1998,** *120,* 9682−9683

Sr_3ARhO_6 (A = Li, Na): Crystallization of a Rhodium(V) Oxide from Molten Hydroxide

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Received December 15, 1997

The oxide chemistry of rhodium reported thus far is completely described by two formal oxidation states, Rh(III) and Rh(IV).[1] No conclusive evidence has been reported for the existence of other oxidation states in rhodium oxides, although lower oxidation states have been reported in organometallic compounds[2] and higher oxidation states have been observed in the fluorides.[3] In this paper, we report the use of molten alkali metal hydroxides as a solvent to stabilize rhodates with a high formal rhodium oxidation state. Two new rhodium(V) oxides have been crystallized at 600 °C in air: Sr_3NaRhO_6 and Sr_3LiRhO_6.

Molten alkali metal hydroxides are a Lux−Flood acid−base solvent system, and are well suited for the synthesis of metal oxides. Since the electrochemical-potential window of the hydroxide melts is large, metals and oxygen exist in various oxidation states.[4,5] Furthermore, the acid−base properties of molten hydroxides can be varied systematically to dissolve and, subsequently, to precipitate metal oxide phases,[4] which provides an opportunity to grow high-quality single crystals.[6] In this case, it appears that molten alkali metal hydroxides provide an environment that stabilizes rhodium oxides with rhodium in the high formal oxidation state of Rh(V). We report below the results of several measurements to verify this assertion, including X-ray diffraction data, electron beam microprobe analyses, thermogravimetric analyses, potentiometric titrations, X-ray photoelectron spectra, and magnetic susceptibility measurements.

The synthesis of Sr_3ARhO_6 (A = Li, Na) was carried out at constant temperature. RhO_2 (0.2 mmol in Rh), $Sr(OH)_2{\cdot}8H_2O$ (7.5 mmol), and alkali-metal hydroxide were added to a silver crucible. $RhCl_3{\cdot}xH_2O$ and Rh_2O_3 are also acceptable rhodium sources. For the synthesis of the sodium containing oxide, 0.25 mol of sodium hydroxide was used. For the lithium analogue, 0.2 mol of $LiOH{\cdot}H_2O$ and 0.1 mol KOH were used; if pure $LiOH{\cdot}H_2O$ was used, the desired product was obtained but was difficult to isolate. The crucible containing the reactants was placed into a furnace that had been preheated to 600 °C. The reaction proceeded at this temperature for 24 h, until crystals precipitated from solution. The molten salt was decanted and the crucible was allowed to cool in a desiccator. After cooling to room temperature, the black crystals (Figure 1) were removed from the residual flux by washing with methanol. Placing the crucible with methanol in an ultrasonic cleaner reduced the time required to dissolve the flux. It also aided in the removal of unreacted RhO_2, which was in the form of a fine powder. The RhO_2 particles were suspended in solution and then poured out of the crucible. This process was repeated until the methanol wash was clear.

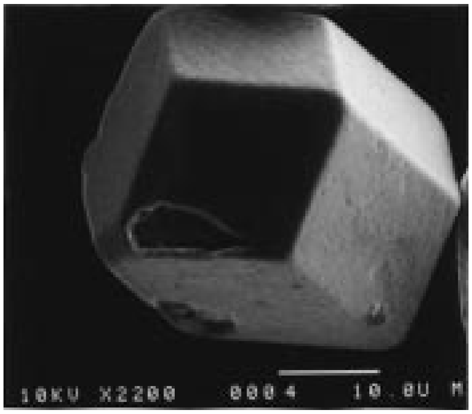

Figure 1. Sr_3ARhO_6 (A = Li, Na) crystals adopt a rhombic dodecahedral habit. Crystal sizes range in size from 0.01 to 0.05 mm.

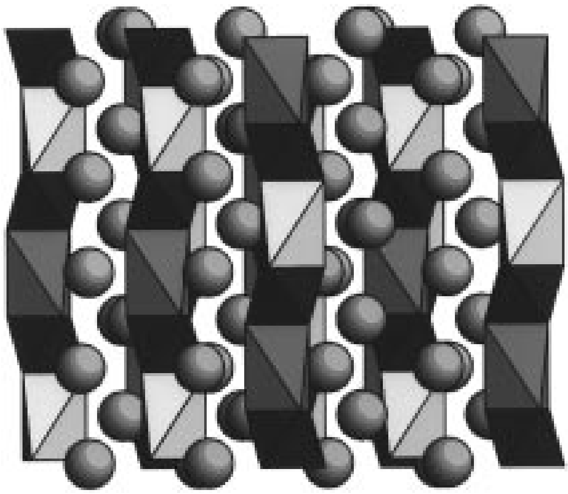

Figure 2. Sr_3ARhO_6 (A = Li, Na) in the K_4CdCl_6 structure type as viewed along the *a*-axis in the hexagonal setting. The material can be described as consisting of $[NaRhO_6]^{6-}$ “chains” parallel to the *c*-axis. These chains consist of Rh^{5+} in octahedral coordination (dark polyhedra) and Na^+ in distorted trigonal-prismatic coordination (lighter polyhedra). The chains are separated by 8-coordinate Sr^{2+} cations (spheres). Although this compound appears to contain 1-dimensional chains, it is better thought of as a three-dimensional material since the interchain Rh−Rh distances are 5.9 Å compared to the intrachain distances of 5.7 Å.

Data from a single crystal of Sr_3NaRhO_6 were collected on a Siemens’ Smart diffractometer. Cell constants of the lithium analogue were obtained by refinement of powder X-ray data collected on a Siemens D5000 diffractometer (Cu Kα radiation) using GSAS.[7] Both phases adopt the idealized K_4CdCl_6 structure-type[8] (Figure 2). Lattice parameters are given in Table 1. The difference in the volume of the unit cell is consistent with the difference in the size of the alkali metal.

The Rh−O bond length is a good measure of the trends in relative oxidation state. On the basis of analysis of the single-crystal diffraction data, the average Rh−O bond length for Sr_3NaRhO_6 is 1.99(2) Å. This can be compared with the Rh−O bond length for rhodium oxides with the same structure type and with A cations of similar size: Na^+ (r = 1.16 Å), Ca^{2+} (r = 1.14 Å), and Gd^{3+} (r = 1.08 Å).[9] The observed bond lengths are

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S0002-7863(97)04231-5 CCC: $15.00

Table 1. Lattice Parameters of Sr_3ARhO_6

A	*a* (Å)	*c* (Å)	*V* (Å^3)
Li	9.6220(4)	11.1544(8)	894.3(1)
Na	9.6036(6)	11.5538(5)	922.8(1)

2.092(12) Å for Rh(III)−O in Sr_3GdRhO_6,[10] 2.026(5) Å for Rh(IV)−O in Sr_3CaRhO_6,[11] and 1.992(8) Å for Rh(V)−O in Sr_3NaRhO_6. This decrease in Rh−O bond length as the charge on the A cation decreases is consistent with an increase in the formal oxidation state of rhodium.

Elemental analyses were performed on a five spectrometer Cameca SX-51 wavelength dispersive electron beam microprobe with a focused beam (2 μm) of high energy (15 keV) electrons. Samples and standards were mounted in epoxy, polished, and then covered with 200 Å carbon. $SrTiO_3$, nepheline, and Rh were used as standards for Sr, Na, O, and Rh. A composition of $Sr_{3.07(9)}Na_{0.92(4)}Rh_{1.00(1)}O_6$ was obtained. This suggests that the material is slightly strontium-rich. Assuming that the samples are fully stoichiometric in oxygen, the microprobe analysis indicates that the formal oxidation state for the rhodium is $Rh^{4.94+}$.

Thermogravimetric analyses were performed on a Shimadzu TGA-50 to determine whether these materials are oxygen deficient. Samples were decomposed by heating at 10 °C/min under flowing H_2 gas according to the following reaction: $Sr_{3.07}Na_{0.92}RhO_{5.9}(s) \rightarrow 3.07SrO(s) + Rh(s) + 0.46Na_2O(s) + 1.10O_2(g)$.

On a freshly prepared sample, a sharp drop in weight of 13.7% was observed at approximately 140 °C. This weight loss was larger than anticipated and is consistent with the loss of both Na_2O and O_2 (13.9% predicted). X-ray powder diffraction on the products indicated the presence of only Rh and SrO. Together with the metals composition determined by microprobe analysis, the observed weight loss is consistent with a composition of $Sr_{3.07}Na_{0.92}RhO_{5.9+d}$ and a formal oxidation state for rhodium of $Rh^{4.74+}$. This value is a lower limit; since Sr_3NaRhO_6 reduces spontaneously air, it is inevitable that some of the sample had already decomposed to Rh(IV) prior to analysis.

Potentiometric titrations were also performed in order to confirm the high formal oxidation state for rhodium. Sr_3ARhO_6 was added to a 1.0 M H_2SO_4 aqueous solution (from distilled, deionized, deoxygenated water) containing Fe^{2+}(aq) in excess of the amount necessary for the reduction of Rh^{5+} to Rh^{3+}. The unreacted Fe^{2+} was titrated with a Ce^{4+}(aq) standard ($(NH_4)_2Ce(NO_3)_6$), and the endpoint was determined potentiometrically. From the total Fe ($Fe^{2+} + Fe^{3+}$) and Fe^{2+} content, the number of electrons transferred from Rh^{5+} to Fe^{2+} was obtained and a formal oxidation state was extracted. The maximum oxidation state observed through potentiometric titrations was $Rh^{4.6+}$. Again, we postulate that this is a lower limit because samples were partially reduced before analysis, and additionally, some oxidation of H_2O occurred during analysis.

Thermogravimetric analyses and potentiometric titrations were performed on both fresh samples and samples that had been exposed to air for times ranging from several days to several months. There was a steady decrease in weight loss measured by thermogravimetric analysis as the sample age increased. A similar trend in number electrons transferred was observed from potentiometric titrations: old samples were observed to contain rhodium in a lower average formal oxidation state than new samples, and powders were less oxidized than crystals. We believe that Sr_3NaRhO_6 is unstable relative to water and that exposure to moisture in the air causes the samples to reduce to Rh(IV).

Table 2. $3d^{5/2}$ Binding Energies for Rhodium Oxides in a Variety of Formal Oxidation States

cmpd	formal oxidation state	binding energy (eV)
Rh_2O_3	3+	308.5
$K_{0.5}RhO_2$	3.5+	308.3
RhO_2	4+	308.6
Sr_2RhO_4	4+	308.5
Sr_3NaRhO_6	5+	310.0, 308.6
Sr_3LiRhO_6	5+	310.7, 309.5

X-ray photoelectron spectroscopy (XPS) was also used to observe trends in oxidation state of rhodium oxides. Data were collected on a Physical Electrons 5400 ECSA system using Mg X-rays ($K_a = 1253.6$ eV). Charging on insulating samples was corrected for by measurement of the position of the C(1s) line from the carbon tape used for mounting. XPS spectra were fit with PHI's data reduction package. The observed Rh($3d^{5/2}$) binding energies are listed in Table 2 for rhodium oxides in various oxidation states. The Rh($3d^{5/2}$) peak for Rh(III) and Rh(IV) containing samples consists primarily of a single large peak at a binding energy of approximately 308.5 eV. A secondary peak of much smaller intensity and centered at higher binding energy (between 309 and 310 eV) was necessary to describe adequately the measured peak. Rh(V) samples were fit with a peak in the range of the Rh(III)/Rh(IV) oxides (308.6, 309.6 eV) and a peak with higher binding energy (310.0, 310.7 eV). Both peaks were of approximately equal area. The marked shift toward higher binding energies is indicative of a more tightly bound electron which is the expectation for a metal in a higher oxidation state. Since XPS is a surface technique, reduction at the crystal surface should also be observable in the XPS spectrum. We attribute the lower energy component of the peak to surface reduction.

Magnetic susceptibility data were collected on a Quantum Design SQUID magnetometer between temperatures of 5 and 380 K at fields of 5 and 40 kG. All samples were cooled in zero field. Above 260 K, there is minimal deviation of the data for Sr_3NaRhO_6 from the Curie−Weiss law ($C \approx 1.5$ emu K mol^{-1}, $\Theta \approx -190$ K). The negative Weiss temperature is indicative of antiferromagnetic ordering. The value of μ_{eff} for Sr_3NaRhO_6 is 2.6 μ_B at 300 K. This is consistent with a low-spin d^4 electron configuration with two unpaired spins. By comparison, μ_{eff} for Sr_3CaRhO_6, a low-spin d^5 system with one unpaired spin, is 1.8 μ_B.[11] Sr_3GdRhO_6, which is d^6, contains no unpaired d electrons, and has an effective paramagnetic moment consistent with only having unpaired f electrons from Gd.[10]

This work represents the first stabilization of a rhodium oxide with a formal oxidation state near Rh(V). While elevated oxygen pressures are required for the synthesis of many Rh(III) and Rh(IV) phases, the Rh(V) phases reported here are obtained by crystallization from molten alkali metal hydroxides at ambient pressure. Metal analysis by microprobe, oxygen analysis by thermogravimetry, oxidation state determination by potentiometric titrations, rhodium−oxygen bond lengths determined by the analysis of single-crystal X-ray diffraction data, and the magnetic moment determined by magnetic measurements are all consistent with a high formal oxidation state for rhodium.

Acknowledgment. Financial support from the National Science Foundation (DMR-9102492) and by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF0009 is gratefully acknowledged. We thank John Donovan for assistance with the collection of the microprobe data, Frank Ogletree for assistance with the XPS, and Ron Wilson for SEM photographs. Thanks are also extended to Johnson-Mattey/Alfa-Aesar for the loan of rhodium through their Precious Metals Loan Program.

JA974231Q

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