Solvothermal Preparation and Control of Phase Composition of Nanosized Rhodium Sulfide Particles

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Well-crystallized Rh_2S_3 and $Rh_{17}S_{15}$ powders with average particle size of 100 nm were solvothermally prepared at 673 K for 10 h with S/Rh ratio of 1.65 and 0.9, respectively. The crystallinity and phase of the rhodium sulfides are closely related to the reaction temperature and the S/Rh ratio. By thermal treatment in Ar, the Rh_2S_3 can be transformed into $Rh_{17}S_{15}$ at 938 K by loss of sulfur.

Rhodium sulfides have attracted more and more attention because of their particular high catalytic activity in hydrodesulfurization[1,2] and oxygen reduction.[3] The rhodium sulfide system contains three phases, Rh_3S_2, Rh_3S_4, and $Rh_{17}S_{15}$, and their bulky products have been obtained at high temperatures above 1300 K.[4–7] The high catalytic activities of rhodium sulfides were closely related to their surface areas and crystalline structures. Rh_2S_3 has a unique layered structure formed by face-sharing pairs of distorted [RhS_6] octahedra, and the layers are loosely bound to each other only by van der Waals forces,[4] while Rh_3S_4 and $Rh_{17}S_{15}$ have structure composed of [RhS_6] octahedra and Rh–Rh metal bonds which give them properties of metallic conductor.[5–7] However, it is still a tough task to prepare well-crystallized rhodium sulfide nanopowders with controlled crystalline phases at low reaction temperatures. Until now, nano-sized rhodium sulfides were mainly synthesized by refluxing[3] and wet chemistry.[8–11] However, these methods only gave amorphous products, and information on the detailed synthesis and phases formed was not provided. In this paper, we provide a simple solvothermal method to prepare nanosized and well-crystallized rhodium sulfide powders. The phase control and thermal behavior evolution of the rhodium sulfides are discussed for the first time according to our best knowledge.

The starting materials were rhodium carbonyl ($Rh_6(CO)_{16}$) and sulfur powder. For a typical reaction to synthesize Rh_2S_3, 0.5 g of $Rh_6(CO)_{16}$ and 0.3 g of sulfur powders (S/Rh molar ratio = 1.65, 10% S in excess) were put into the autoclaves and solvothermally treated in xylene at temperatures from 493 to 673 K for 10 h. The products were harvested by centrifuge, washed with acetone, and finally dried at 353 K for characterization. The thermal treatments were conducted at temperatures from 673 to 1023 K in Ar atmosphere. The morphologies and structures were characterized by X-ray diffraction (XRD, Rigaku RTP-300 RC), transmission electron microscopy (TEM, JEOL JEM-2010). The TG-DTA (Seiko TG/DTA 6300) was conducted in N_2 atmosphere.

Figure 1 shows the XRD patterns of the products obtained at different temperatures with S/Rh ratio of 1.65. Well-crystallized rhodium sulfide Rh_2S_3 was synthesized at 673 K (JCPDS No: 35-0736, Figure 1a). The reaction at 623 K gave poorly crystallized Rh_2S_3 (Figure 1b), while the reaction at low temperatures

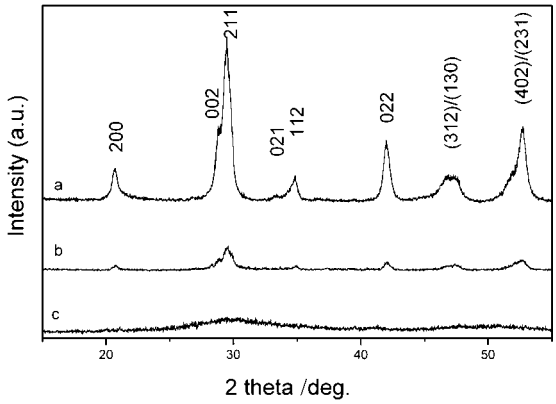

Figure 1. XRD patterns of Rh_2S_3 powders synthesized at different temperatures (S/Rh = 1.65). a) 673 K for 10 h; b) 623 K for 10 h; c) 493 K for 10 h.

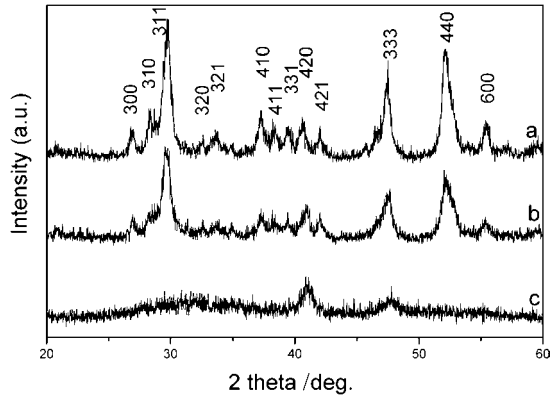

Figure 2. XRD patterns of $Rh_{17}S_{15}$ powders synthesized at different temperatures (S/Rh = 0.9). a) 673 K for 10 h; b) 623 K for 10 h; c) 493 K for 10 h.

below 493 K resulted in formation of amorphous products (Figure 1c). Crystalline $Rh_{17}S_{15}$ was also formed at 673 K with S/Rh ratio of 0.9 (JCPDS No: 73-1443, Figure 2a), and the reaction at 623 K gave poorly crystallized products (Figures 2b and 2c). HRTEM pictures of Rh_2S_3 and $Rh_{17}S_{15}$ synthesized at 673 K show clear lattice fringes. The particle size of the Rh_2S_3 powder prepared at 673 K is about 100 nm (Supporting Information, Figure S1).[12]

The growth mechanism of the rhodium sulfides in solvothermal reaction can be explained by a dissolution–precipitation process, because both rhodium carbonyl and sulfur are separately dissolved in xylene under solvothermal conditions, and the nanosized rhodium sulfides have quite different morphology from that of dozens of micron-sized bulky rhodium carbonyl

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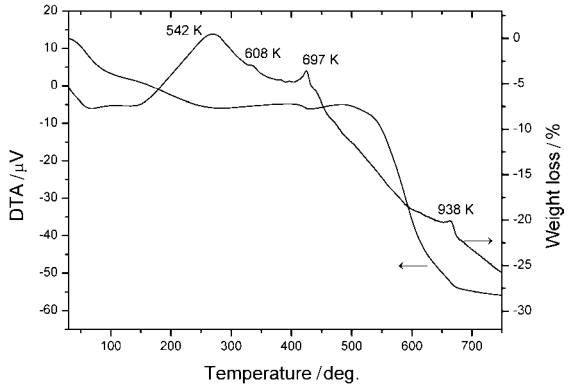

Figure 3. TG-DTA results of the amorphous rhodium sulfide powders prepared at 493 K for 10 h (S/Rh ratio = 1.65).

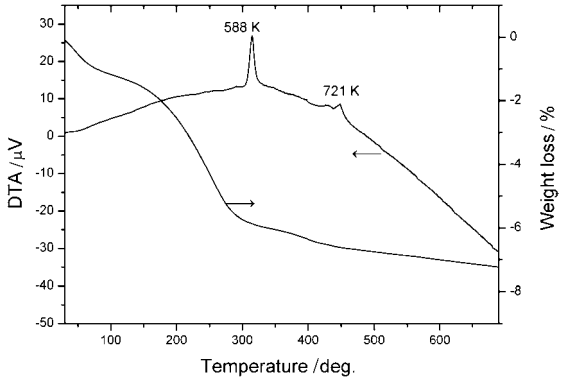

Figure 4. TG-DTA results of the amorphous rhodium sulfide powders prepared at 493 K for 10 h (S/Rh ratio = 0.9).

crystals. Good crystallinity of the rhodium sulfides needs high reaction temperature up to 673 K for more than 2 h under solvothermal conditions (we use 10 h in our experiments to make sure the complete reaction). The amorphous rhodium sulfides obtained at 493 K can also crystallize by calcination at 673 K. The S/Rh ratio affects the crystallization after calcination. Especially for Rh_2S_3, too excessive sulfur content in the starting materials can produce sulfur abundant rhodium sulfide that has poor crystallinity even after calcination at 673 K (Supporting Information, Figure S2).

The TG-DTA measurements were conducted for the amorphous Rh_2S_3 and $Rh_{17}S_{15}$ powders prepared at 493 K. For Rh_2S_3 powders, the weight loss up to 623 K accompanied by two exothermic peaks at 542 and 608 K is ascribed to the decomposition of the organic compounds (Figure 3). For the exothermic peaks at 697 K, we ascribed it to the crystallization of Rh_2S_3 since the XRD results show that amorphous rhodium sulfide synthesized at 493 K can be crystallized to Rh_2S_3 by calcinations at 673 K in Ar (Supporting Information, Figure S3a). It is also observed that a large weight loss occurs at around 873 K owing to the release of sulfur. Accompanied by this weight loss, an exothermic peak appears at 938 K in the DTA curve, which corresponds to the phase formation of $Rh_{17}S_{15}$. This phase formation is supported by the XRD pattern of product calcined at 1023 K for 5 h in Ar (Supporting Information, Figure S3b). The calcined rhodium sulfide is pure $Rh_{17}S_{15}$. The total weight loss up to 1023 K is about 28.2%.

For the amorphous $Rh_{17}S_{15}$ powder (Figure 4), two exothermic peaks were observed at 588 and 721 K in the DTA curve, in which the exothermic peak at 588 K corresponded to the decomposition of the organic compounds, while the exothermic peaks at 721 K was ascribed to the formation of $Rh_{17}S_{15}$ phase because the XRD results show that amorphous rhodium sulfide synthesized at 693 K can be crystallized to $Rh_{17}S_{15}$ by calcinations at 713 K in Ar (Supporting Information, Figure 3c). The large weight loss of the amorphous Rh_2S_3 at around 873 K is not observed in amorphous $Rh_{17}S_{15}$. After calcination at 1023 K for 5 h in Ar, the product is still pure $Rh_{17}S_{15}$ (Supporting Information, Figure 3d).

In conclusion, both Rh_2S_3 and $Rh_{17}S_{15}$ crystalline powders are prepared for the first time by solvothermal reaction at 673 K. They consist of fine particles with average particle size of 100 nm. The crystallinity and phase composition of the rhodium sulfides are closely related to the reaction temperature and the S/Rh ratio. During heat treatment in Ar, the Rh_2S_3 can be transformed into $Rh_{17}S_{15}$ at 938 K by loss of sulfur. These rhodium sulfides are expected to present high catalytic activities in hydrodesulfurization and oxygen reduction reaction.

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References and Notes

1 R. Oviedo-Roa, J.-M. Martinez-Magadan, F. Illas, *J. Phys. Chem. B* **2006**, *110*, 7951.
2 A. Tan, S. Harris, *Inorg. Chem.* **1998**, *37*, 2215.
3 R. W. Reeve, P. A. Christensen, A. J. Dickinson, A. Hamnett, K. Scott, *Electrochim. Acta* **2000**, *45*, 4237.
4 E. Parthé, E. Hohnke, F. Hulliger, *Acta Cryst.* **1967**, *23*, 832.
5 J. Beck, T. Hilbert, *Z. Anorg. Allg. Chem.* **2000**, *626*, 72.
6 S. Geller, *Acta Cryst.* **1962**, *15*, 1198.
7 H. R. Naren, A. Thamizhavel, A. K. Nigam, S. Ramakrishnan, *Phys. Rev. Lett.* **2008**, *100*, 026404.
8 I. B. Rufus, V. Ramakrishnan, B. Viswanathan, J. C. Kuriacose, *Langmuir* **1990**, *6*, 565.
9 M. Cattenot, J.-L. Portefaix, J. Afonso, M. Breysse, M. Lacroix, G. Perot, *J. Catal.* **1998**, *173*, 366.
10 E. J. M. Hensen, H. J. A. Brans, G. M. H. J. Lardinois, V. H. J. de Beer, J. A. R. van Veen, R. A. van Santen, *J. Catal.* **2000**, *192*, 98.
11 Y.-M. Tsou, H. Deng, G. N. Martelli, R. J. Allen, E. S. De Castro, U.S. Patent 141108, **2002**.
12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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