Synthesis and Magnetic Properties of Mesoporous Vanadium Oxide Sulphate

Shigemi Kohiki,* Hirokazu Shimooka, Syozo Takada, Akihiko Shimizu, Tomohiro Hirakawa, Seiji Takahashi, Hiroyuki Deguchi,† and Masaoki Oku††
Department of Materials Science, Kyushu Institute of Technology, Tobata, Kita-kyushu 804-8550
†*Department of Electrical Engineering, Kyushu Institute of Technology, Tobata, Kita-kyushu 804-8550*
††*Institute of Materials Research, Tohoku University, Sendai 980-8577*

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Preparation and magnetic properties of mesostructured $VOSO_4$ based materials, which were synthesized using liquid-crystal templating technique, have been investigated. Low temperature magnetic properties of the samples exhibited Langevin paramagnetism with an effective magnetic moment $\mu_{eff} \fallingdotseq 1.4\,\mu_B$ and a paramagnetic Curie point $\theta \fallingdotseq 0$ K without any magnetic transition, which were considerably different from magnetic properties of α- or β-$VOSO_4$ crystals.

Since reporting of new family of porous materials (MCM-41) with periodic mesopores of 30–40 Å by liquid-crystal templating technique, various mesoporous materials have been synthesized using similar templating method.[1] Whereas mesoporous materials have attracted much attention in a viewpoint of catalyst, we take an interest in those mesoporous materials as templates for quantum dots or wires.[2–4] Vanadium oxide sulphate has two types of polymorphs, i.e. α-$VOSO_4$ and β-$VOSO_4$, which show different magnetic properties.[5,6] α-$VOSO_4$ has a tetragonal structure with chains along c axis consisted of corner-shared VO_6 octahedra connected by corner-shared SO_4 tetrahedra. V–O distance along c axis is considerably different; thus VO_6 octahedra regard as VO_5 pyramid which forms lamellar structure. It is known that the α-type crystal is ferro- or ferrimagnetic below 4 K and $\theta = -12$ K. β-$VOSO_4$ has an orthorhombic structure with zigzag chains of distorted VO_6 octahedra connected by SO_4 tetrahedra to form a three-dimensional network. β-$VOSO_4$ shows antiferromagnetic behaviors with a Néel point $T_N = 25$ K due to their V–SO_4–V superexchange interaction. Since both α- and β-$VOSO_4$ crystals have features of structural flexibility based on the connection by corner sharing of distorted VO_6 and SO_4 units, changes of magnetic properties are expected with changes of the oxidation state and local structure. Thus, if we can prepare mesostructure using crystalline or amorphous $VOSO_4$ by means of molecular templating technique, novel magnetic properties associated with decreasing dimension are expected. In this paper, we report synthesis and magnetic properties of mesoporous $VOSO_4$ based materials for the first time.

Mesoporous $VOSO_4$ based materials were synthesized using $VOSO_4 3.5H_2O$ (Kishida Chemical Co., Ltd.), *n*-cetyltrimethylammonium chloride $C_{16}H_{33}(CH_3)_3NCl$ (designated as C_{16}TMA, Tokyo Kasei Kogyo Co., Ltd.) and H_2O with a molar ratio of 1 : 1.1 : 92.8. A solution obtained by mixing of the raw materials was dried at 130 °C in air. XRD pattern of a sample as dried is shown in Figure 1a. Several peaks were observed at $2\theta = 2.24°$ (d = 43.8 Å), 4.16° (23.6 Å), 6.06° (16.2 Å) and 8.23° (12.0 Å), while no peaks at $2\theta > 10°$ were observed. This result indicates mesoscopic periodic structure of amorphous vanadium based materials formed along the template of surfactant micelles.

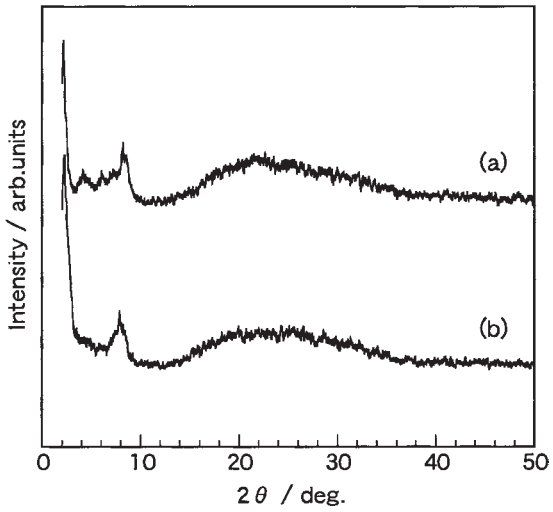

Figure 1. XRD patterns of a sample as dried with C_{16}TMA (a) and mesoporous $VOSO_4$ based material heat-treated at 300 °C in flowing N_2 (b).

Condition of thermal treatment to remove surfactant without degradation of periodic mesostructure in flowing N_2 was examined using TG-DTA as shown in Figure 2. Weight loss accompanied by endothermic reaction around 70 °C, which was attributed to desorption of adsorbed water, was observed. Other weight losses accompanied by endothermic reaction around (1) 150–290 °C, (2) 320–390 °C and (3) 410–560 °C attributed to

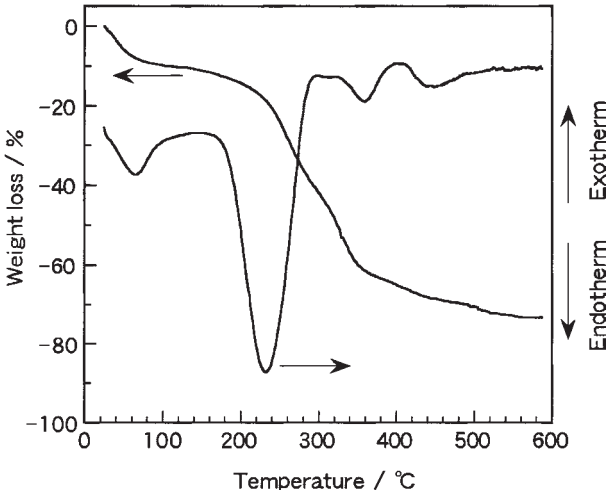

Figure 2. TG-DTA curves of a sample as dried with C_{16}TMA in flowing N_2.

thermal decomposition of surfactant were also observed. This figure indicates that thermal treatment above 560 °C is necessary to remove the surfactant completely. On the other hand, from the elimination of peaks around $2\theta = 2°$ in the XRD measurement, it was confirmed that the periodic mesostructure of the sample had already been damaged at 400 °C. Therefore, in this paper, characterization of a sample fired at 300 °C which still retained periodic mesostructure with XRD peaks at $2\theta = 2.30°$ (d = 38.4 Å), 7.81° (d = 12.6 Å) as shown in Figure 1b was carried out, in spite of a half surfactant remained in the sample. From XPS measurement, N 1*s*, C 1*s* and S 2*p* peaks besides V and O peaks were observed, but no Cl peaks were observed. Moreover, as shown in Figure 3, the binding energies of V $2p_{3/2}$ and S 2*p* are in good agreement with that of $VOSO_4$ and SO_4^{2-}, respectively.[7] Hence, the partially mesoporous vanadium based material fired at 300 °C consists of amorphous $VOSO_4$ network and residual organic component without vanadium oxychloride.

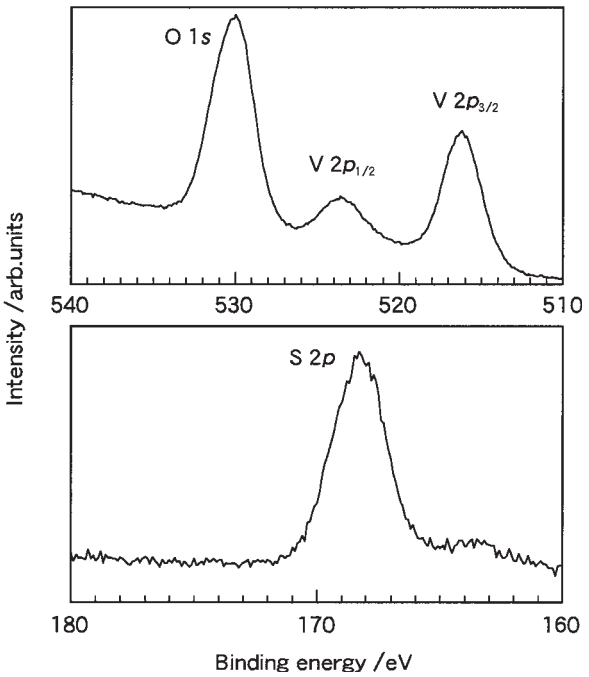

Figure 3. O 1*s*, V 2*p* and S 2*p* XPS spectra of mesoporous $VOSO_4$ based material heat-treated at 300 °C in flowing N_2.

Figure 4 shows temperature dependence of reciprocal molar magnetic susceptibility measured by SQUID for the samples as-dried and fired at 300 °C. Number of moles of vanadium per 1 g of both samples were 1.64×10^{-3} mol and 2.82×10^{-3} mol, respectively, when a sample fired at 560 °C was assumed to be an anhydrous $VOSO_4$. As shown in Figure 4, both samples obey Curie-Weiss law with $\theta \fallingdotseq 0$ K. This indicates that both the samples exhibit Langevin paramagnetism with free spins, which is different from α- or β-$VOSO_4$ crystal. Effective magnetic moments μ_{eff} of both samples were $\mu_{eff} = 1.41\,\mu_B$ and $1.43\,\mu_B$, respectively. Since the values are close to theoretical spin-only value of V^{4+} ($3d^1$) ($\mu_{eff} = 1.73\,\mu_B$), oxidation number of

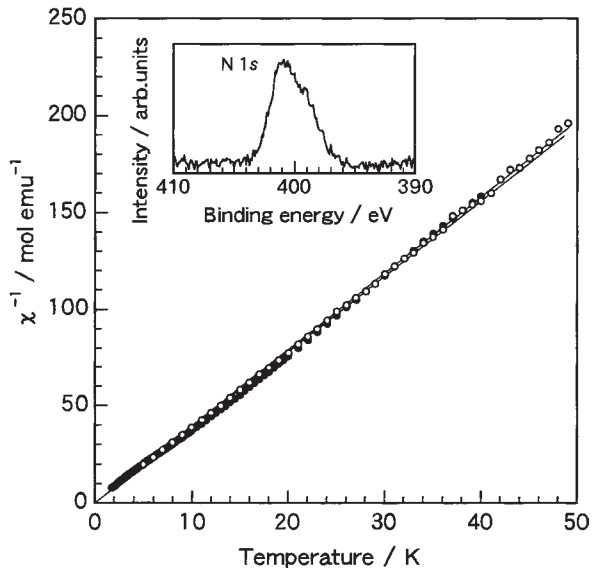

Figure 4. Reciprocal molar magnetic susceptibility vs temperature curves: ◯ a sample as dried with C_{16}TMA; ● mesoporous $VOSO_4$ based material heat-treated at 300 °C in flowing N_2. Inset: N 1*s* XPS spectrum of the latter sample.

vanadium in both samples are considered to be V^{4+} ($3d^1$). However, deviation from the theoretical value is considerably larger than that of α-$VOSO_4$ ($\mu_{eff} = 1.69\,\mu_B$) and β-$VOSO_4$ ($\mu_{eff} = 1.54\,\mu_B$) crystals with V^{4+} ($3d^1$).[5,6] The reasons are as follows; viz. a portion of oxygen of surface V–S–O network are thought to be substituted by nitrogen of surfactant due to large surface area attributed to mesostructure, which indicate existence of V^{5+} ($3d^0$). This assumption is based on the fact that broad peak which consists of the peaks more than two with different binding energies was observed in XPS spectrum of N 1*s* as shown in inset of Figure 4. In addition, this assumption may indicate that the elimination of magnetic transition in both the samples is attributed to hindrance of V–SO_4–V superexchange interaction by V^{5+}.

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