

Ultrasonic-assisted synthesis of highly dispersed MoO₃ nanospheres using 3-mercaptopropyltrimethoxysilane

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Abstract

With ultrasonic irradiation as assistance, highly dispersed MoO₃ nanospheres were synthesized using silane coupling agent 3-mercaptopropyltrimethoxysilane HS-(CH₂)₃Si(OCH₃)₃ (MPTS) as figuration agent. The results of X-ray powder diffractometer (XRD) showed that the precursor was hexagonal molybdenum oxide hydrate (MoO₃ · 0.55H₂O). It was converted into orthorhombic MoO₃ after annealed at 400 °C for 2 h. Transmission electron microscopy (TEM) showed that MoO₃ · 0.55H₂O and MoO₃ nanoparticles were spherical with particle-size distribution of ca. 30–80 nm and 25–75 nm, respectively. Results indicated that MPTS and ultrasonic irradiation played important role in formation of highly dispersed MoO₃ nanospheres. X-ray photoelectron spectroscopy (XPS) was also adopted to confirm the growth mechanism. The possible cause of formation was based on dispersion function of ultrasonic irradiation and figuration of MPTS.

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1. Introduction

In recent years, the “chemistry of form” has attracted considerable interest in chemistry and materials science. Nanomaterials with novel morphologies were believed to have some better performance than bulk materials. A promising route to synthesize nanomaterials with definite morphologies is to use appropriate templates. For this point, a great deal of research dealt with preparation and characterization of nanostructured inorganic materials with various templates were reported [1–6].

At the same time, the studied inorganic materials have extended to semiconductors, catalysts, superparamagnetic materials and biominerals. Many of them show particle-size and modified-surface dependence in physical and chemical properties. Among them, MoO₃ with nanosize was attractive for its wide application. It is not only an important electrochromic- and photochromic-sensitive material for optical device applications [7–9], but also a promising material for photoelectrochemical energy production, with high surface area having higher photo efficiencies [10,11]. MoO₃ was known well as one of the most widely used catalysts [12–14]. Its catalytic efficiency has long been known, e.g. in alcohol and methane [15,16]. And it was also good precursor for synthesizing many other important materials, such as MoS₂, MoSe₂, Mo and host–guest compounds [17–20].

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Recently, remarkable progress has been achieved concerning preparation of molybdenum trioxide to optimize its physical and chemical properties, especially catalysis. To have an optimum catalytic performance, certain “design criteria” must be fulfilled by the catalyst material [21,22], among which uniform distribution of the catalytic plays an important role in its catalytic activity. With this perspective, endeavors in the fabrication methods have been made to ensure good dispersion of molybdenum catalyst to improve catalyst performance [21,23]. Aiming at enhancing the dispersion, MoO_3 is commonly dispersed on high surface area “inert” carriers such as Al_2O_3 , MgO or SiO_2 [24,25]. Among which, well-dispersed SiO_2 supported MoO_3 was prepared effectively by ultrasonic irradiation of a slurry containing $\text{Mo}(\text{CO})_6$ and nanometer silica spheres.

Ultrasound irradiation is a conventional method to prepare nanoparticles and shows a rapid growth in its application to prepare nanomaterial due to its desirable reaction effects. The chemical effects of ultrasound arise from the acoustic cavitation: formation, inflation and implosive collapse of bubbles in liquid. Bubble collapse generates the hot spots with intense local heating, high pressures, and extremely cooling rates which can promote the reaction rate and control the particle-size. Up to now, MoO_3 nanostructures synthesized sonochemically were also reported by many researchers [21,23,25,26]. In those works, ultrasound plays an important role in decomposing the $\text{Mo}(\text{CO})_6$ and accelerating the reaction rate.

In this present work, we report a rapid synthesis of highly dispersed MoO_3 nanospheres using 3-mercaptopropyltrimethoxysilane $\text{HS}-(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ (MPTS) as the figuration agent via an ultrasonic irradiation procedure. The final product is composed of very uniform particles both in size and in shape. The average particle-size is ca. 60 nm with narrow particle-size distribution. Effects of ultrasound, 3-mercaptopropyltrimethoxysilane, PH value and adding speed of the acid on the nucleation and growth of MoO_3 nanospheres were also discussed. Compared with the conventional methods via a template (for example: silica nanospheres), it is not necessary to consider the surface interactions and coating problems in our synthesis path. The highly dispersive characteristic and spherical morphology of MoO_3 nanoparticles could increase the whole surface area, which may improve the photo and catalytic efficiency greatly. And the highly dispersed spherical MoO_3 nanoparticles are suited for synthesizing spherical-like IF- MoS_2 material with ultra-low friction coefficient [27] and we have received prospective effect presently. In addition, such a synthetic pathway is expected to be used to synthesize other inorganic nanospheres with highly dispersive characteristic.

2. Experimental section

All the reagents used in this experiment, were of analytical grade and used as received. For the synthesis of MoO_3 ,

Silane coupling agent, 3-mercaptopropyltrimethoxysilane (MPTS) were added into the anhydrous toluene ($\text{C}_6\text{H}_5\text{CH}_3$) and mixed with stirring. Then 0.05 mol/L ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ with water as the solvent added into the mixture at rate of 15 s/drop, under mechanical agitation and ultrasonic (40 kHz, 300 W) for 2 h at room temperature. Then dilute hydrochloric acid (HCl) was dropped into the solution via a dropping funnel until the PH reached about 2.5. The system was stirred and irradiated with ultrasonic for another 30 min. After the chemical reaction finished, the resultant was separated by a centrifuge, air dried, and washed with deionized water several times. After dried again at 70 °C in a vacuum drying oven for 6 h, a light-blue sample was obtained. Then the precursor was heated at 400 °C for 2 h in a muffle furnace with color of the sample changing to white.

Several techniques have been used to characterize the as-synthesized samples. The crystal structure of the samples was determined using a standard X-ray powder diffractometer (XRD, Rigaku D/max-rA) with $\text{CuK}\alpha$ radiation. The morphology and microstructure of the samples were investigated by transmission electron microscopy (TEM, JEM-2000EX for Fig. 2a, b, g and h and Hitachi-H8100 for Fig. 2d and e). The surfaces of the samples were characterized by X-ray photoelectron spectroscopy (XPS) on Surface Science Instruments X-probe and M-probe spectrometers using monochromatic Al K R X-ray sources ($h\nu = 1486.6$ eV).

3. Results and discussion

Fig. 1 shows the XRD pattern of the precursor without annealing and the product synthesized at 400 °C for 2 h. According to the results of Fig. 1a, the reflections are close to hexagonal molybdenum oxide hydrate ($\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$), with lattice constants $a = 10.581$ Å, $c = 3.720$ Å (JCPDS card No. 48-399). Fig. 1b reveals that the product is composed of high-purity MoO_3 nanoparticles. All the reflections can be indexed to orthorhombic MoO_3 , with lattice constants $a = 3.945$ Å, $b = 13.848$ Å, and $c = 3.690$ Å (JCPDS card No. 76-1003). The $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ was annealed at different temperature and results indicated that $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ was converted into MoO_3 till the temperature reached 400 °C.

The morphology investigations were characterized by TEM, operated at 200 kV. A TEM image of the typical product (Fig. 2a) showed that MoO_3 nanoparticles were dispersed and no aggregation was observed. The magnified image (Fig. 2b) showed these MoO_3 nanoparticles were entirely spherical with diameters of ca. 25–75 nm. The corresponding particle-size distribution of MoO_3 nanospheres was presented in Fig. 2c and the average particle-size was ca. 60 nm. The images of $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ are shown in Fig. 2d and 2e. Obviously, the spherical nanoparticles have already formed before the sample was annealed. Compared to the MoO_3 , the particle-size distribution of the $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ exhibited larger diameters of ca. 30–80 nm (Fig. 2f) and some even exceeded 100 nm

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