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Synthesis of V_2O_5 Nanoparticles in Reverse Micelles[1]

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Abstract—20–40 nm vanadium(V) oxide nanoparticles have been prepared via reverse micelles method using sodium dodecyl sulfate as surfactant, ethanol and ethyl acetate as additives, water as disperse phase, and hexane as continuous phase. V_2O_5 has been formed via ammonium metavanadate under acid hydrolysis. The so obtained nanoparticles have been characterized by ultraviolet-visible spectroscopy, infrared spectroscopy, atomic force microscopy, and matrix-assisted laser desorption ionization mass spectrometry.

Keywords: ammonium metavanadate, vanadium(V) oxide, reverse micelle, nanoparticles, template synthesis, hydrolysis

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Reverse micelles method has been widely used for synthesis of monodisperse nanoparticles. Reverse micelle solution is a colloid system with liquid polar phase dispersed in liquid non-polar continuous phase, the disperse phase being stabilized by surfactant at the interphase boundary. The microscopic disperse phase may act as nanoreactor for production of various nanoparticles [1, 2].

V_2O_5 nanoparticles have been recognized for excellent catalytic properties. Nanosized catalysts are extremely efficient and selective in heterogeneous catalysis due to the high specific surface [3]. Activity of catalytically active nanoparticles often strongly depends on their size and shape. V_2O_5 nanorods and nanospheres have revealed superior catalytic performance as compared to bulk V_2O_5 [4] and have been therefore used to catalyze a number of organic transformation such as oleic acid ozonolysis [5], thiophene hydrodesulfurization [6], etc.

Preparation of V_2O_5 nanoparticles using cetyltrimethylammonium bromide micellar solution has been reported in [4]. The 45–160 nm nanoparticles have been obtained with ammonium metavanadate and sulfuric acid as precursors. In the present study, we report on another reverse micelle system applier for preparation of V_2O_5 nanoparticles, based on sodium dodecyl sulfate. The synthesis of V_2O_5 nanoparticles was performed by mixing two reverse micelles solutions. Collision of nanodroplets of acidic micelles 1 and of NH_4VO_3-containing micelles 2 led to the reactants interaction according to the following scheme:

$$2VO_3^- + 2H^+ \rightarrow V_2O_5 + H_2O.$$

The precipitation took place inside the nanodroplets and gave the primary nanoparticles; the subsequent ripening processes (growth and coagulation) yielded the final product. The surfactant molecules adsorbed at the particles surface prevented their further aggregation and preserved them in the finely dispersed state.

Electronic absorbance spectrum of the prepared product revealed absorption band at 350–400 nm typical of yellow solution of V_2O_5 nanoparticles [7] (Fig. 1).

IR spectrum of the product (Fig. 2) revealed characteristic absorption bands at 956 cm^{-1} (V=O stretching) and 587 cm^{-1} (V–O–V stretching) [8–11]. The broad absorbance band centered at 3391 cm^{-1} was attributed to stretching of hydroxyl group, and the band at 1625 cm^{-1} was assigned to bending vibrations of water molecules; those bands evidenced about the presence water molecules adsorbed at the surface of V_2O_5 nanoparticles. Other bands (with maximums at 1400 and 1746 cm^{-1}) were assigned with carbonate and carboxylate groups appearing due to the contact of the product with atmosphere [12].

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[1] The text was submitted by the authors in English.

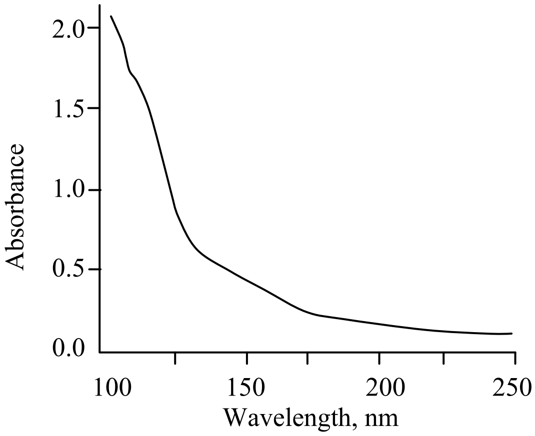

Fig. 1. Electronic absorbance spectrum of the prepared nanoparticles solution.

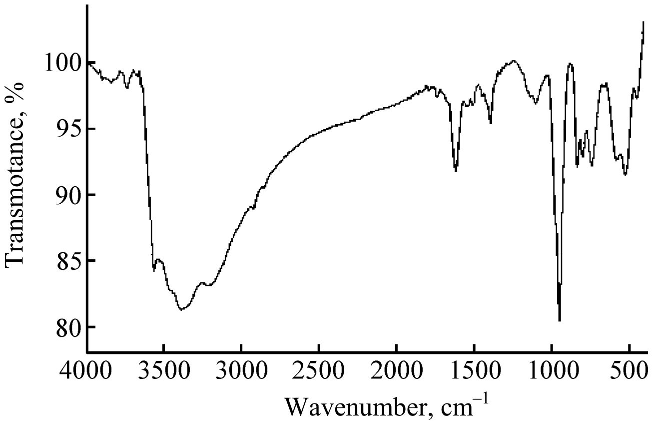

Fig. 2. Infrared spectrum of the prepared nanoparticles.

Atomic force microscopy study of the product revealed that the formed 20–40 nm nearly spherical aggregates consisted of much smaller particles (Fig. 3). Evidently, the small particles correspond to the primary product of the reaction inside the collided micelles, whereas the aggregates resulted from the subsequent ripening of the precipitate.

MALDI mass spectrum of V_2O_5 nanoparticles (Fig. 4) contained the base peak at 189.931 *m*/*z* assigned to the $V_2O_4Na^+$ ion. Accurate assignment of other peaks requires further experiments. To conclude, we managed to prepare spherical V_2O_5 nanoparticles via reverse micelle method. The particles composition was confirmed by several spectroscopy methods. AFM observation revealed that the 20–40 nm particles were aggregates of smaller primary particles formed inside the micellar reactor.

EXPERIMENTAL

Ammonium metavanadate, sulfuric acid, sodium dodecyl sulfate, hexane, ethanol, and ethyl acetate were purchased from Sigma-Aldrich and used as received.

Two micellar solutions (solution 1 and solution 2) were prepared separately.

Solution 1. 3 mL of H_2SO_4, 80 mL of water, and 7 mL of aqueous solution of sodium dodecyl sulfate (4 g) were stirred during 15 min. 10 mL of ethyl acetate, 50 mL of ethanol, and 250 mL of hexane were then slowly added in sequence to the mixture upon continuous stirring.

Solution 2. 2.98 g of NH_4VO_3 was dissolved in 80 mL of water at 60°C, and then 7 mL of aqueous solution of sodium dodecyl sulfate (4 g) was added dropwise upon continuous stirring over 15 min. 10 mL of ethyl acetate, 50 mL of ethanol, and 250 mL of hexane were then slowly added in sequence to the mixture upon continuous stirring.

Nanoparticles preparation. The solutions 1 and 2 prepared as described above were stirred during about 10 min until semitransparent solutions were formed, and then solution 1 was poured into solution 2 upon continuous stirring. The obtained mixture was further stirred during 30 min at 45°C, a brownish-orange solution of V_2O_5 nanoparticles was obtained. The mixture was left overnight at room temperature for evaporation of organic solvents. The nanoparticles were centrifuged off the aqueous medium and washed with ethanol and water. The yellow nanoparticles were dried at 75°C and then annealed at 600°C during 4 h in a furnace.

Electronic absorbance spectrum was obtained using a UV-Visible double beam spectrophotometer (Thermo

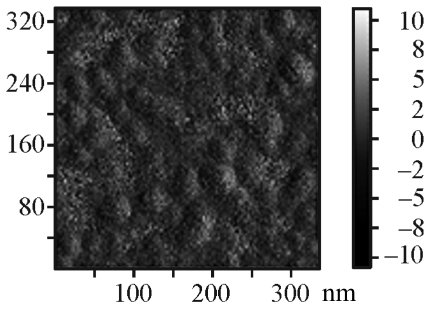

Fig. 3. Atomic force microscopy image of the prepared nanoparticles.

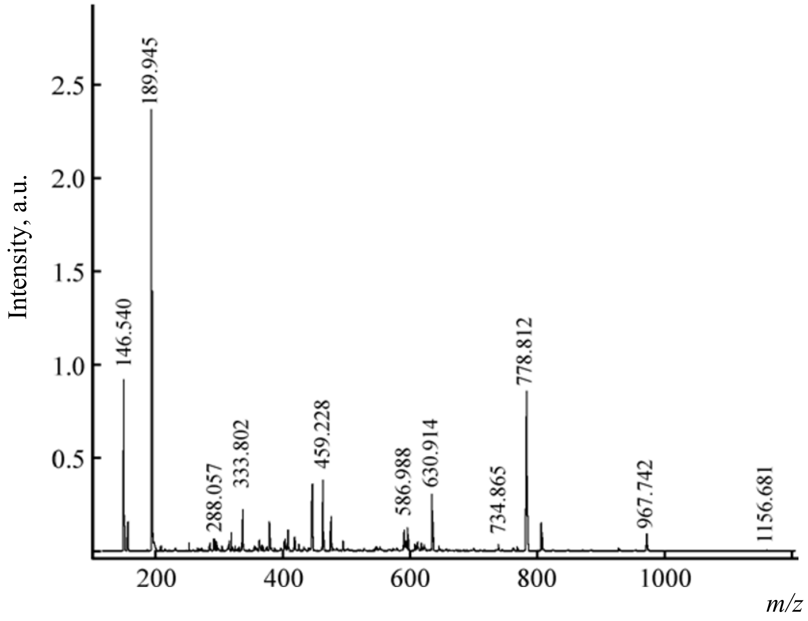

Fig. 4. MALDI mass spectrum of the prepared nanoparticles.

Scientific Evolution 300, UK). The specimen was prepared as follows. 1.05×10^{-4} mol/L solution of V_2O_5 nanoparticles in deionized water was sonicated during 15 min until formation of a uniform dispersion of nanoparticles. The absorption spectrum was immediately recorded using a 1 cm quartz cell with water as reference.

Transmittance FT-IR spectrum was recorded at 400 to 4000 cm^{-1} using a VECTOR 22 spectrometer. The specimen was prepared as follows. About 5 mg of dried V_2O_5 nanoparticles were mixed with pure solid KBr powder and pressed into a pellet under pressure of 400 torr.

Atomic force microscopy imaging was carried out using an Agilent technologies 5500 AFM device. The specimen was prepared as follows. 1.05×10^{-4} mol/L V_2O_5 nanoparticles solution in deionized water was sonicated during 15 min; a drop of the solution was immediately spread on a freshly cleaved mica surface and left for two days in a dust-free environment.

MALDI mass spectra were recorded using an Ultraflex III TOF/TOF instrument (Bruker Daltonics). The specimen was prepared as follows. 5.52×10^{-4} mol/L solution of V_2O_5 nanoparticles in deionized water was sonicated during 15 min. 1 μL of the solution of V_2O_5 nanoparticles and 5 μL of α-cyano-4-hydroxycinnamic acid were loaded onto a sample plate and allowed to dry. After drying, the sample plate was put into the mass spectrometer, and the spectrum was recorded with 600 shots of a nitrogen laser (337 nm) in reflectance mode.

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