Synthesis of finely divided molybdenum sulfide nanoparticles in propylene carbonate solution

Pavel Afanasiev *

Institut de recherches sur la catalyse et l'environnement de Lyon UMR5256, CNRS-Université de Lyon 1, 2 avenue Albert Einstein, Villeurbanne Cedex 69626, France

ABSTRACT

Molybdenum sulfide nanoparticles have been prepared from the reflux solution reaction involving ammonium heptamolybdate and elemental sulfur in propylene carbonate. Addition to the reaction mixture of starch as a natural capping agent leads to lesser agglomeration and smaller size of the particles. Nanoparticles of MoS_x ($x \approx 4$) of 10–30 nm size are highly divided and form stable colloidal suspensions in organic solvents. Mo K edge EXAFS of the amorphous materials shows rapid exchange of oxygen to sulfur in the molybdenum coordination sphere during the solution reaction. Thermal treatment of the amorphous sulfides MoS_x under nitrogen or hydrogen flow at 400 °C allows obtaining mesoporous MoS_2 materials with very high pore volume and specific surface area, up to 0.45 cm^3/g and 190 m^2/g, respectively. The new materials show good potential for the application as unsupported hydrotreating catalysts.

© 2014 Published by Elsevier Inc.

1. Introduction

Molybdenum sulfide MoS_2 is one of the most studied materials in various fields of science, including tribology [1], hydrotreating catalysis [2], photo/electro catalysis [3,4], field emission [5] and microelectronics. Preparation of nanoparticulate molybdenum sulfide materials is widely investigated and was recently reviewed [6]. A myriad of techniques were explored, arguably encompassing the whole palette of the existing approaches to inorganic materials synthesis and including such versatile techniques as hydrothermal [7], solvothermal [8], sol–gel [9], mechanochemical [10], ionic liquid—assisted [11,12], precursor decomposition [13,14] and others. The incentive to develop new preparation techniques comes from the interest to novel large scale and simple syntheses with improved control of particles morphology. With this respect solution methods represent an attractive way of preparation, since homogeneous or seed-induced nucleation in the solutions leads to narrower size distributions. Beside the quality of materials, the requirements to the synthetic procedure are important. The preferred techniques should be environmentally friendly and use non-toxic reagents. Any synthesis of an inorganic sulfide must necessarily involve a source of sulfur. Among the sulfur containing compounds the cheapest and the most benign is rhombic elemental sulfur S_8. Sulfur can be dissolved in many organics and in

principle can be readily used for syntheses. However to make it react the temperature should be somewhat increased, in order to break the S–S bonds. Thus, earlier, we applied sulfur melts in the range 300–400 °C to prepare molybdenum sulfide [15]. Alternatively, elemental sulfur can react with molybdenum species upon reflux in an organic solvent, if the temperature can be raised high enough. Such reactions are particularly attractive since they can be implemented using simple laboratory glassware, without recourse to hydrothermal equipment. Recently we studied the solution reaction in ethylene glycol which allows replicating of cellulose morphology by molybdenum sulfide [16]. However in the absence of a template or a seed, the particles of molybdenum sulfide grown in ethylene glycol are rather large (> 300 nm) and strongly agglomerated. Moreover sulfur solubility in ethylene glycol appears to be quite limited. Therefore an alternative solvent should be proposed for better morphology control. In this work we report on the novel reaction using propylene carbonate and allowing solution preparation of small and weakly agglomerated molybdenum sulfide nanoparticles.

2. Experimental

2.1. Preparation of solids

In a typical experiment 1.6 g (0.05 g/at S) of sulfur S_8 and 0.75 g (0.004 g/at Mo) ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$

* Corresponding author. Tel.: +33 472445466.
  E-mail address: pavel.afanasiev@ircelyon.univ-lyon1.fr

were added to 75 mL of propylene carbonate (PC) upon vigorous stirring. Eventually 2 g of potato starch was added to the same mixture as a capping agent. The reaction mixture was rapidly heated to the boiling point of PC and kept upon stirring for different time from 15 min to 2 h. Then the reaction mixture was cooled and diluted with 200 mL of ethanol. Solid product was separated by centrifugation, washed twice with absolute ethanol and dried in air.

Thermal treatment was carried out in a flow of nitrogen or hydrogen at a mass flow rate 56 and 4 h^{-1}, respectively. The solids were heated to 400 °C at a linear rate 10 ° min^{-1} in a Pyrex reactor. After thermal treatment the solids were kept and handled under inert atmosphere.

2.2. Characterizations

The X-ray diffraction (XRD) patterns were obtained on a Bruker diffractometer with Ni-filtered Cu $K\alpha$ radiation, recorded in the range of 2θ between 3° and 80°. Crystalline phases were identified with standard ICDD files. Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010 instrument. Pore size distributions in the mesopores domain were calculated using Barrett–Joyner–Hallenda (BJH) method. Prior to measurements the samples were heated in a secondary vacuum at 300 °C for 4 h. Molybdenum content in the synthesized solids was determined after dissolution in a HNO_3/H_2SO_4 mixture by plasma-coupled atomic emission spectroscopy (AES-ICP). The sulfur, carbon and hydrogen contents were measured with a CHNS-O EUROEA300 elemental analyzer. The reaction products in the liquid were identified by GC–MS (Hewlett Packard 5973/6890 system). EPR spectra were recorded at 77 K on a Bruker ESP 300E spectrometer using (TE102) EPR cavity (Bruker ER4102ST) at microwave power 1.6 mW and modulation amplitude 3 G. Hydrodynamic size distribution of particles was measured using Dynamic Light Scattering (DLS) on a Wyatt Nanostar device. Prior to measurement the powders were ultrasonically dispersed in absolute ethanol. Suspensions containing about 0.5 g/L of solids were applied for the DLS measurements. Size distribution was obtained from averaging of a series of 100 single measurements 2 s each. Autocorrelation function was cut below 1.5 and above 1000 nm.

The morphology of the particles was examined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) on a JEOL 2010 microscope with an accelerating voltage of 200 kV. For TEM and HRTEM analysis, the as-synthesized nanoparticles were first dispersed in ethanol by ultrasonic treatment. Then, a drop of the dispersion was transferred to a holey carbon film supported on a copper grid and evaporated naturally. Size distribution histograms were built using Digital Micrograph software by Gatan. Size distributions were obtained for particles that do not strongly overlap and can be visually distinguished.

X-ray absorption spectroscopy (XAS) experiments were carried out at the BM30b (CRG-FAME) beamline of the ESRF synchrotron facility [17]. The Mo K-edge spectra were measured in the transmission mode, using a Si(2 2 0) crystal monochromator. The data were treated using FEFF [18] and VIPER [19] programs. The edge background was extracted using cubic spline. Extended X-ray absorption fine structure (EXAFS) fitting was done in the R and k spaces. Coordination numbers (CN), interatomic distances (R), Debye–Waller parameter (σ^2), and energy shifts (ΔE_0) were used as fitting variables. Constraints were imposed on the parameters in order to keep them in the physically reasonable ranges.

2.3. Catalytic tests

Thiophene HDS tests carried out without exposure of the solids to oxygen, the solids were transferred to the catalytic microreactor under argon. Steady state activities after 12 h on stream were compared at 300 °C, at atmospheric pressure. The temperature varied between 280° and 340 °C in order to measure kinetics and to build Arrhenius plot of the reaction rate. The products were analyzed using on-line gas chromatography. Reaction rate was determined using pseudo-first rate equation assuming large excess of hydrogen. In the chosen temperature range, 280–340 °C, the thiophene conversion was below 10% under the conditions used (partial pressure P_{thio}=2.7 kPa; 50 mL/min gas flow, 100–150 mg of catalyst). The specific reaction rate Vs, was calculated according to equation.

$$Vs = -(F/m)\ln(1-x)$$

where F is the thiophene molar flow (mol/s), m is the catalyst mass (g), and x is the thiophene conversion.

3. Results and discussion

3.1. Solution reaction

Prior to the syntheses of sulfides, we briefly studied mutual reactivity of the couples of ingredients in the reaction mixtures. To do so, we carried out several qualitative tests by putting into the reaction simplified combinations of reactants, in order to get an idea of the solubility and to check whether the ingredients react with each other.

Hot PC readily dissolves all loaded sulfur and forms intensely yellow transparent solution which does not visually change at least for 1 h. Sulfur solubility in hot PEC, exceeds 50 g/L at its boiling temperature. Homogeneous yellow solution was formed upon mixing 50 mL PEC with 1.6 g of S_8 at ca 180 °C.

By contrast ammonium heptamolybdate (AHM) appeared to have low solubility in PC. When heated alone with PC, AHM does not dissolve but the liquid phase changes its color from white to yellowish and then to brown, suggesting progressive reduction of Mo(VI) to lower oxidation degrees. The solubility of AHM at 100 °C determined as the difference of mass before and after prolonged stirring in PC at room temperature was less than 1 g/L. Heating above 100 °C leads to dehydration of AHM and to its progressive reduction, which hinders accurate determination of solubility. Formation of intensely colored solution upon reflux suggests that reduced molybdate species are better soluble in PC than the initial AHM. Electron spin resonance of the solutions probes taken while heating ammonium heptamolybdate in PC confirms that molybdenum is reduced to the Mo(V) species. Indeed an intense and broad signal was observed at the g factor near 1.97, typical for the Mo(V) oxospecies (not shown). The intensity of the ESR signal grew with the reaction time from 2×10^{16} spins/cm after 10 min to 9.10^{16} spins/cm for 1 h. This corresponds to 5–10% of the whole molybdenum loaded being in a reduced and dissolved form. We can therefore conclude that AHM as such does not dissolve readily in PC, but molybdenum is released to the solution as Mo(V). More detailed study of the individual reactivity between PC and AHM was beyond the scope of this work.

When starch and sulfur were heated together in PC, pale yellow turbid suspension was formed. No complete solubilization of starch in PC was obtained. After cooling the mixture, starch powder decantated and sulfur needles re-crystallized on the reactor walls. No signs of reaction between sulfur and starch were noticed within 1 h of reflux.