Colloids and Surfaces A: Physicochem. Eng. Aspects 469 (2015) 202–210

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Colloidal and microemulsion synthesis of rhenium nanoparticles in aqueous medium

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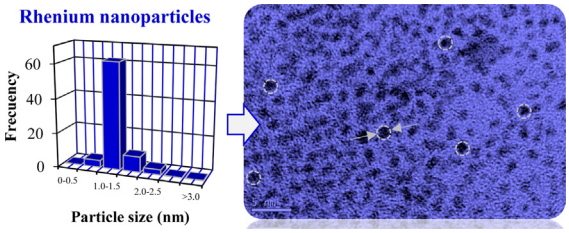
HIGHLIGHTS

- Re nanoparticles synthetized by simple colloidal and micremulsion method in aqueous medium.
- Higher mean size range for colloidal (0.7–2.8 nm) than for microemulsion synthesis (0.7–1.4 nm).
- Low size and narrow distribution achievable by slow addition of reducing agent.
- Faster/easier reduction and higher size observed for synthesis at high temperature in inert atmosphere.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 12 January 2015
Accepted 18 January 2015
Available online 28 January 2015

Keywords:
Rhenium
Nanoparticles
Colloidal synthesis
Microemulsion synthesis

ABSTRACT

Rhenium nanoparticles (Re NPs) were synthesized by simple colloidal and microemulsion methods in aqueous medium under air and inert atmosphere. Colloidal synthesis using PVP as protective agent and $NaBH_4$ as reducing agent led to pseudo-spherical Re NPs with mean size in the range of 0.7–2.8 nm. The effect of the synthesis temperature, the reducing agent addition rate, and the capping and reducing agent to Re ratio on the particle size and particle distribution was studied. In the presence of air, the synthesis at 60 °C provided faster and more complete reduction, however reoxidation was observed once the reducing agent was consumed. The reoxidation was avoided removing the oxygen dissolved in the water medium by bubbling N_2 or H_2. The increase of the synthesis temperature in the range studied (10–80 °C) resulted in a higher mean particle size and a more heterogeneous particle size distribution. A slower addition rate of the reducing agent produced Re NPs with more homogeneous size, together with some reduction of the mean particle size. An increase in the amount of reducing agent at high temperature, 70–80 °C, resulted in the formation of agglomerates of large size, apparently formed by smaller nanoparticles. The increase of the PVP to Re molar ratio from 10 to 40 resulted in some narrowing of the particle size distribution. The synthesis of Re NPs was also achieved for a water-in-oil microemulsion system (*n*-heptane/AOT) under inert atmosphere using $NaBH_4$ as reducing agent. The mean size (0.8–1.4 nm) and size distribution of the pseudo-spherical Re nanoparticles were found to be affected mainly by the water to surfactant ratio. Under all the conditions and synthesis procedure tested Re showed a trend to produce rather small nanoparticles in comparison to other metals.

1. Introduction

The preparation of nanoparticles of transition metals has been extensively studied in diverse fields including optical [1,2], catalytic [3,4], and electronic [5] applications. However, the literature

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http://dx.doi.org/10.1016/j.colsurfa.2015.01.031
0927-7757/

contains few references on the synthesis of nanoparticles of group 7 transition metals, namely Mn, Tc and Re. Specifically, a broad range of hi-tech applications have been reported for Re and Re alloys. Re has the second highest melting point (3185 °C) among all metals, exceeded only by W (3422 °C) [6]. This property makes rhenium a very promising raw material for different practical applications that require high temperature-resistant materials, such as the manufacture of jet engine components, improving engine life, performance and operating efficiency [7]. Furthermore, taking into account its low standard reduction potential of 0.3 V [6], pure Re nanoparticles could be used in the preparation of alloy nanocomposites by galvanic replacement [8,9]. Applications in medicine, such as magnetic targeted radiotherapy, have been studied for Re-188 labeled onto the surface of silica-coated magnetite nanoparticles [10].

With regard to the applications in catalysis, Reis crucial in catalyzing petroleum reforming reactions at ca. 500 °C and 15 atm [11]. The Re catalysts have been found to be resistant to poisoning by sulfur and carbon monoxide [12,13]. Important expectations have been laid on Re and Pt–Re catalysts in the aqueous phase reforming of biomass materials [14,15]. Carbon supported bimetallic Re-Pt catalysts have also shown potential in reduction reactions such as the removal of perchlorate in water [16].

In spite of the potential above mentioned, the preparation of Re nanoparticles has rarely been studied in the literature . One of the main drawbacks for the development of methods for the synthesis and application of Re NPs is the instability of the Re colloids generated by chemical reduction. Early studies on the reduction of the perrhenate ion in water indicated the uncertain nature of the reduction products due to oxidation by air and the occurrence of mixed oxidation states [17]. Mucaloet al. [18,19] studied the preparation of Re colloids by chemical reduction of K_2ReCl_6 in water by N_2H_4 and $NaBH_4$, both in the absence and presence of protective agents, observing that the NPs are highly susceptible to rapid reoxidation to oxidation states that are even higher than that of the starting hexachlororhenate ion. This behavior has as an additional consequence the uncertainty about the influence of the synthesis conditions on the distribution of oxidation states.

To inhibit the oxidation by atmospheric oxygen during the preparation of Re NPs, different procedures have been studied, generally based on non-aqueous solvents. Revina et al. [20] reported on the synthesis of Re nanoparticles in reverse micelles (water/isooctane). Both the use of γ-radiation chemical reduction in anaerobic conditions and the use of flavonoids (quercitin and dihydroquercitin) as reducing agents resulted in positive reduction results, as supported by monitoring of the reaction medium by spectrophotometry and atomic force microscopy (AFM) measurements showing NPs with sizes between 1 and 12 nm. Chong et al. [21] synthesized rhenium nanoparticles by pulsed-laser decomposition of ammonium perrhenate (NH_4ReO_4) or dirheniumdecacarbonyl ($Re_2(CO)_{10}$) in the presence of 3-mercaptopropionic acid(MPA) as capping agent, in both aqueous and organic media. The use of laser decomposition was claimed as essential to avoid the formation of intermediate complexes that makes difficult further reduction. However, large mean sizes (35–40 nm) and a high size dispersion of the Re nanoparticles was found for this method. The MPA-capped Re nanoparticles prepared by this method were capable of catalyzing the isomerization of 10-undecen-1-ol to internal alkenols. Gyger et al. [22] developed a synthesis procedure based on reverse micelles of liquid ammonia in oil. The polarity of the ammonia phase makes possible to use conventional inorganic Re precursors, although to achieve the formation of reverse micelles temperatures of −40 °C were required. The use of reducing agents such as sodium thiosulphate was found lo lead to the formation of rhenium sulfide NPs with an average size of 5.5 nm that can be applied in radiotherapy [23].

Regarding water-free reaction media, Zinn [24] reported a method to produce Re NPs in organic media using rhenium chloride (V) as precursor, *n*-dodecylamine as capping agent and $NaBH_4$ as reducing agent. The method was mainly focused on the preparation of Re NPs for metallurgical applications, claiming that a wide range of Re NPs (4–100 nm) can be obtained modifying the proportions of the different chemicals involved in the synthesis. Yurkov et al. [25] produced Re NPs by thermal decomposition of $Re_2(CO)_{10}$, $Re_4O_6(OCH_3)_{12}$ and NH_4ReO_4 in matrix of low-density polyethylene, thus obtaining a metal-containing composite. Chong and Fan [26] showed that Re_2O_7 methanol solution placed within two silicon wafers can be reduced at 250 °C producing well dispersed ReO_3 nanocubes. Recently, Ayvali et al. [27] reported on the synthesis of Re NPs by reduction of $[Re_2(C_3H_5)_4]$ under a H_2 atmosphere at 3 bar and 120 °C for two days in anisole as a solvent, using hexadecylamine or polyvinylpyrrolidone as stabilizing agent. Monodisperse Re NPs with a particle size of ca. 1.0–1.2 nm, denoted as ultra-small, were obtained.

The current work reports for the first time on a systematic study of the synthesis of Re NPs in water or water in oil medium using simple colloidal and microemulsion synthesis methods. The influence of the synthesis variables is studied for the sake of producing stable and size-controlled Re NPs suspensions.

2. Experimental

2.1. Materials and methods

Potassium hexachlororhenate (IV), K_2ReCl_6 (99.99%), ammonium perrhenate, NH_4ReO_4 (99.999%), sodium borohydride, $NaBH_4$ (98%), polyvinylpyrrolidone (PVP) with an average mol. wt. of 40,000 g/mol, methanol (≥99.9%), heptane (99%) and dioctyl sodium sulfosuccinate (AOT, 98%) were purchased from Sigma Aldrich and used without further purification. All the experiments were performed using water deionized by a Mili-Q water purification system.

In a typical colloidal synthesis experiment, 5 mL of a 0.02 M solution of K_2ReCl_6 or NH_4ReO_4 in water was prepared. Additionally different amounts of PVP were dissolved in 20 mL of distilled water. The amounts of PVP dissolved were adjusted in order to obtain PVP:Re molar ratios between 10 and 40. Afterwards, both solutions were mixed and heated or cooled to the reaction temperature, which varied between 10 and 80 °C. In some cases a high purity flow of hydrogen or nitrogen was bubbled to the mixture to remove the oxygen dissolved in the water in order to avoid oxidizing conditions. Finally, 5 mL of a $NaBH_4$ aqueous solution was introduced dropwise under vigorous stirring to prepare a Re hydrosol in which PVP served as stabilizer. The $NaBH_4$ to Re molar ratio was maintained in the 10–50 range. The Re hydrosol was stirred for 2 h after the addition of the reducing agent to allow complete reduction.

For the microemulsion synthesis experiments, water/AOT/*n*-heptane microemulsion was prepared according to Moulik et al. [28]. Rhenium nanoparticles were obtained by reduction of a microemulsion containing K_2ReCl_6 with other with $NaBH_4$. Firstly, 0.016 mmol of K_2ReCl_6 and 100 μL deionized water mixed with AOT dissolved in *n*-heptane. Secondly, another microemulsion containing 0.1 mmol of $NaBH_4$, 100 μL of water and AOT dissolved in n-heptane was prepared. The amount of AOT in each experiment was fixed to achieve water to AOT ratios (w_0) ranging from 1 to 8 (mol/mol). The two microemulsions were mixed and stirred at 35 °C and under hydrogen atmosphere for 1 h to achieve Re reduction and avoid the reoxidation. The resulting microemulsion containing the Re nanoparticles was placed in a rotary evaporator (Büchi) at 65 °C and under vacuum to remove the solvent. Finally, the nanoparticles were purified three times by resuspension in 25 mL of methanol