IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

ONE-STEP SYNTHESIS OF GOLD NANOPARTICLES STABILIZED IN ACID-ACTIVATED MONTMORILLONITE FOR NITROPHENOL REDUCTION

F. Ammari[*], S. Sakrane and M. Chenouf
[*] Department of chemical process engineering, Ferhat-Abbas Sétif-1 University, Sétif, Algeria

ABSTRACT

Gold nanoparticles were prepared by one-step using chemical reduction from $HAuCl_4.3H_2O$ gold precursor by sodium borohydride ($NaBH_4$) in presence of acid-activated montmorillonite us stabilizer. The obtained gold nanoparticles stabilized in montmorillonite (Au°-montmorillonite) were used as catalysts for reduction of 4-nitrophenol to aminophenol with sodium borohydride at room temperature. Different techniques (UV-Vis spectroscopy, XRD, TEM and N_2 adsorption) were used to characterize gold nanoparticles. The UV-Vis results confirmed directly the gold nanaoparticles formation. The XRD, N_2 adsorption and MET results was also confirmed the formation of gold nanoparticles in the pores of montmorillonite with an average size of 5.7nm with uniform distribution. The reduction reaction of 4-nitrophenol into 4-aminophenol with $NaBH_4$ catalyzed by Au°-montmorillonite catalyst exhibits remarkably a high activity; the reaction was completed within 4.5min.

KEYWORDS: 1. Gold 2. Montmorillonite 3. Nanoparticles 4. Chemical reduction method 5. 4-nitrophenol

INTRODUCTION

Recently, synthesis of metal nanoparticles has attracted significant attention because of their important application in nanotechnology. The metal nanoparticles have been used for optical [1] and electronic fabrication [2], sensors production [3] and as catalysts [4-6]. In particular, synthesis of gold nanoparticles (AuNPs) has attracted much attention since the pioneering discovery of the high catalytic activity of supported gold nanoparticles in the reaction of CO oxidation at low temperature [7]. For example gold catalysts have been used in CO oxidation [8], water-gas shift reaction [9], selective hydrogenation [10, 11] and nitro-aromatic reduction [12]. Among reactions of nitro-aromatic reduction, the reduction of 4-nitrophenol to 4-aminophenol is an important reaction in the preparation of analgesic and antipyretic agent such as paracetamol [13]. Apart from this; this reaction is mostly used us a reaction model for testing the gold nanoparticles reactivity [14-16]. It was found, that the formation of small AuNPs enhanced the catalytic activity of this type of catalyst, at the other hand, their activity tend to decreased because of the aggregation of nanoparticles. In general the use of stabilizer or efficient support is required to prevent the AuNPs from aggregating. The stabilization of AuNPs has been performed by using polymers [17, 18] or surfactants [19]. Moreover, it was found that using metal oxides such as MgO [20], TiO_2 [21] or Al_2O_3 [22] leaded to the formation of small AuNPs, and this is feasible without addition of any stabilizer. Recently clays minerals have been attracted much attention because of their environmentally benign, cost and abundance. Deposition of highly dispersed small AuNPs on the surfaces of montmorillonite and sepiolite was reported by Zhu et al. [23], on the other hand, Letaief et al. [24] confirmed that AuNPs can be deposited on the external surface on the external surface of sepiolite, moreover they found that the control of gold particle size can be achieved by controlling the acidic pre-treatment conditions of this clay mineral. Borah et al. [25] indicated the stabilization of gold nanoparticles in montmorilllonite porosity; they found that variation in acid activation conditions of montmorillonite leaded to changing her specific area and then affected significantly the size of gold particle. In this research field, we used montmorillonite pre-acidified under gentle conditions for gold nanoparticles stabilization in liquid phase by chemical reduction method with some modification compared to reduction method reported in literature. Here gold nanoparticles were simply prepared in one-step using sodium borohydride as reductant agent and montmorillonite as stabilizer. In this study, the catalytic reduction of 4-nitrophenol by gold nanoparticles stabilized on montmorillonite using $NaBH_4$ as reductant agent was investigated. Moreover the resulting samples; acid-activated montmorillonite and gold-montmorillonite were characterized by several methods, UV-Vis spectroscopy, X-ray Diffraction

(XRD), transmission electron microscopy (TEM) and N_2 adsorption.

Reagents

For samples preparation, natural bentonite, obtained from the Roussel deposit of Maghnia (Algeria), was used as gold-stabilizer after treatment of purification and acidification with HCl, $HAuCl_4.3H_2O$ (Sigma Aldrich) as gold precursor, $NaBH_4$ (Sigma Aldrich) as reductant agent and 4-nitrophenol (Fisher Chemical) for catalytic test. All other reagents were used as received without further purification.

Acid activated montmorillonite preparation

Purification and homoionisation

Natural bentonite was purified by sedimentation to remove impurities like sand feldspar and calcite. Typically, 10 g of bentonite was vigorously stirred in 1l of distilled water for 3 h and kept 24h for sedimentation. The portion corresponding to 2/3rd of uppermost portion supernatant was then separated and dried overnight at 80°C, finally the samples were powdered. After sedimentation step, the purified bentonite mainly montmorillonite were transformed to the homoionic Na-exchanger form by treatment with 1M sodium chloride solution, after centrifugation and washing of samples for several times a <2nm fraction of Na-montmorillonite were collected and designed as Na-mont.

Acidification

For maintaining undamaged structure of Na-mont, the treatment of acidification was obtained under gentle conditions. 5g of Na-mont was treated with 50ml of 4M HCl for 2h at room temperature, then the acidified Na-mont was washed several times with distilled water before drying overnight at 60°C, the collected acid activated sample was designed as Amont.

Gold nanoparticles preparation

The 2wt% Au stabilized in acid-activated montmorillonite (Amont) was prepared by one-step reducing 10ml of $HAuCl_4.3H_2O$ solution (0.05mmol Au) with 10ml of $NaBH_4$ aqueous solution (4mmol) in presence of 10ml of Amont suspension (0.5g). The $NaBH_4$ solution was added slowly and the mixture was kept under vigorous stirring for 1h at room temperature. After centrifugation and washing of three times with distilled water, the samples were dried overnight at 60°C and the collected samples were designed as Au-Amont. The preparations and storage were performed in the absence of light.

MATERIALS AND METHODS

Catalytic reduction of 4-ntrophenol (4-NP)

The 4-nitrophenol reduction was carried out in liquid phase at room temperature. Typically, 10ml of $NaBH_4$ (10mmol) aqueous solution was added to 10mg of Au-Amont (0.2mg Au) previously dispersed in 10ml of distilled water, at this mixture 10ml of aqueous solution of 4-NP (0.1mmol) was added under vigorous stirring. The molar ratio of Au:4-NP:$NaBH_4$ used in this reaction was 1 :100 :10000. Since the excess amount of $NaBH_4$ used for reduction reaction, the reaction rates can be regarded as being independent of the concentration of $NaBH_4$, consequently, the reaction order was supposed pseudo first-order to 4-NP[14]. The reduction process was monitored by UV-Vis absorption spectrometry. Avery 90s, 1ml of reaction suspension was filtrated and then injected into quartz cuvette of UV-Vis spectrometer. In the UV-Vis spectra, the absorption at 398 nm corresponds to 4-NP, whereas the absorption at 298 nm corresponds to 4-aminophenol (4-AP), the reaction product.

Characterization

UV-Vis absorption spectra were recorded on SHIMADZU UV-170 spectrometer, BET surfaces areas and pore diameter were obtained using a Micromeritics Tristar II machine and pore diameter was calculated from BJH method. The XRD analyses were performed on X'Pert Pro PANanalytical instrument using CuKα radiation, transmission electronic microscopy (TEM) observation were carried out on TOPCON-002B apparatus, all samples were dispersed in ethanol solution and then deposited on a holey carbon film supported on copper grid.

RESULTS AND DISCUSSION

Characterization results

UV-Vis spectrometry results immediately confirmed the gold nanoparticles formation by suspension of gold-montmorillonite analysis during preparation**.** A large band centred at 520nm corresponding to small gold particles was observed (Fig.1.). The same band was observed by Borah et al. [25] and C. Lin et al. [26].

BET results (Table 1) show that surface area of Na-mont increased from 55.8 to 74.5m^2/g after acidification, but significant decrease of surface area was observed for Au-Amont sample with a surface area of 13.3m^2/g. The diameter pore value confirmed the presence of mesopores on A-mont samples.

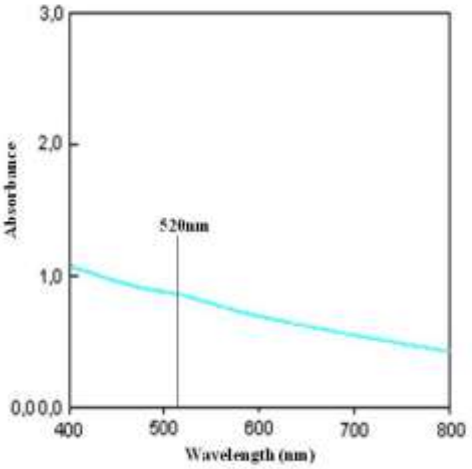

Fig. 2 Adsorption-desorption isotherms of 2%Au-mont

Table 1. BET results

Samples	Na-mont	Amont	Au-Amont
BET(m^2/g)	55.8	74.7	13.3
Pore diameter (nm) (BJH) model		8.5	

In addition the adsorption-desorption isotherms reported in Fig. 2 of mont was of type-IV following IUPAC classification with presence of H3 hysteresis, indicating mesoporous solid.The decrease in surface area on Au-Amont can be attributed to nanoparticles gold stabilization within the mesopores of acidified montmorillonte.

The XRD analysis on A-mont and Au-Amont are reported in Fig.3a.

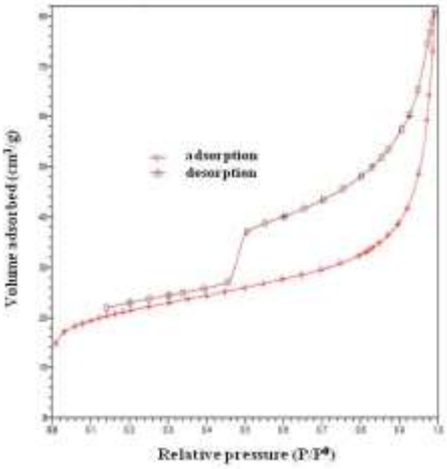

Fig. 2 Adsorption-desorption isotherms of 2%Au-mont

The insertion of gold nanoparticles into montmorillonite was also confirmed by the XRD analysis, in addition to typical montmorillonite diffraction peaks, four characteristic gold reflections were, Au(111) at 38.2°, Au(200) at 44.5°, Au(220) at 64.6° were observed. XRD spectra of Au-Amont reported in 33-40° 2Theta regions (Fig.3b) was used to calculate gold particles size. A gold particles size estimated by XRD analysis is about 6nm.

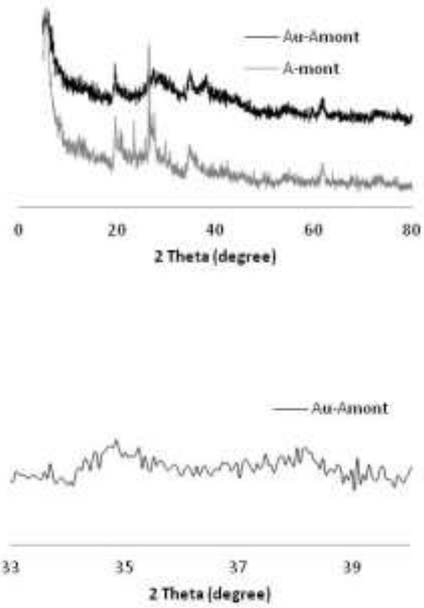

Fig.3. XRD analysis on Amont comprared to Au-Amont in 2-80 2Theta region (a), and XRD spectra Of Au-Amont in 33-40 2Theta region (b).

In the TEM (Fig.4.) images, the gold particles appeared as homogeneously dispersed on the A-mont stabilizer. The sizes of most particles are about 3-7nm with average particle size of 5.7nm, same (smaller fraction) are as large as 9nm.

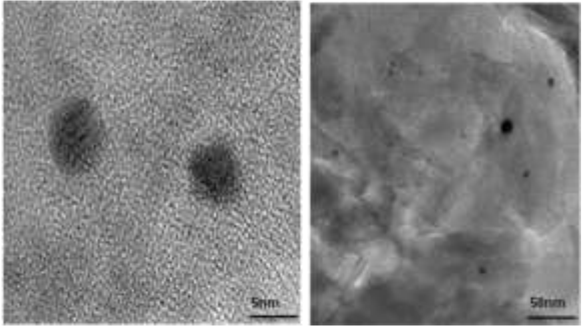

Fig.4. TEM image of overview of Au-Amont

4-nitrophenol reduction

The catalytic activity of gold nanoparticles in Au-Amont was investigated for 4-NP reduction to 4-AP, the reaction was monitored by UV-Vis spectrometry. The UV-Vis analysis results are reported in Fig.5a. The absorbance at 398nm corresponds to 4-NP decreased, whereas a new peak with absorbance at 298 nm appeared, this absorption corresponds to 4-AP.

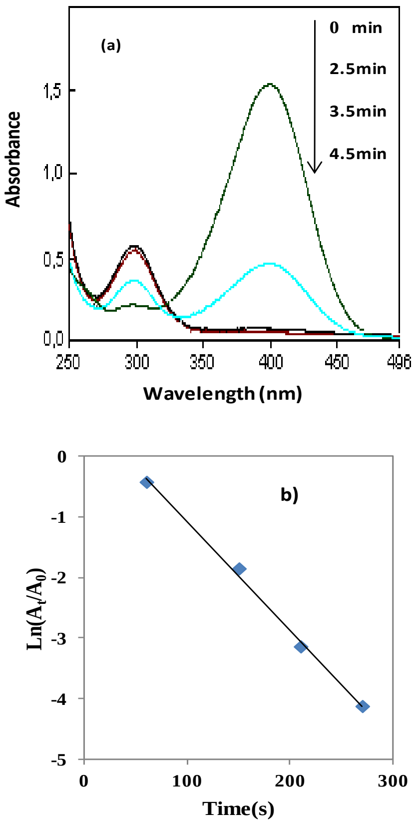

Fig.5. UV-Vis absorption spectra for 4-NP reduction on Au-Amont with an excess of $NaBH_4$ at room temperature (a). Plot of ln(A_t/A_0) versus reaction time of reduction (b).

The characteristic peak of 4-AP increased rapidly and the reaction was completed within 4.5min. The Au-Amont was very active for this reaction type, no reduction activity was observed on the stabilizer (Amont) alone or without Au-Amont catalyst presence. From the absorbance data, Fig.5.b show the variation of the ln(A_t/A_0) versus reaction time, where A_0 and A_t are the initial absorbance of 4-NP and the absorbance of 4-NP at reaction time, t, respectively. A good linear correlation has been obtained and a calculated value of rate constant is about 1.79 10^{-2} s^{-1}, this result confirmed the high activity of Au-Amont catalyst in the reaction of 4-nitrophenol reduction.

CONCLUSION

In the present study, gold nanoparticles AuNPs were successfully prepared in one-step by using a facile preparation method in presence of acid-activated montmorillonite as stabilizer agent. The stabilizer agent Amont was prepared by first purification then acid treatment with HCl in gentle conditions. The characterisation results confirmed the small gold nanoparticles formation within the mesopores of Amont. The catalytic activity of the synthesized Au-Amont was investigated for 4-nitrophenol with an excess amount of $NaBH_4$. The reaction followed a pseudo-first-order rate with a constant rate of 2.18 10^{-2} s^{-1}, this result confirmed the high activity of Au-Amont in 4-NP reduction. This work represents gold nanaparticles synthesis in one-step by a simple method using acid-activated montmorillonite for gold nanoparticles stabilization, this facile preparation can be used for other metal nanoparticles preparation.

ACKNOWLEDGEMENTS

The authors thank Dr. S. Ivanova (Instituto de Ciencia de Materiales de Sevilla, Spain) for N_2 adsorption and XRD characterization and T. Dintzer from ICPEES (Institute of Chemistry and Processes for Energy, Environment and Health, Strasbourg University, France) for MET analyses.

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AUTHOR BIBLIOGRAPHY

Fatima Ammari born in Medjana Algeria), received her Engineering degree at Ferhat-Abbas sétif-1 University of Algeria, in 1998, was the winner of the national contest in Chemical Engineering BAF (1998) and got a 4 years of scholarship in France. **S**he obtained the PhD title in Chemistry from Louis Pasteur University of Strasbourg, France, in 2002 in Laboratoire de Matériaux, Surface et Procédés Catalytiques (LMSPC), CNRS-ECPM.Currently she is a Senior Lecturer in the Department of Chemical Process Engineering, Ferhat-Abbas Sétif-1 University, Dr Ammari's research integrates engineering, applied chemistry, materials, catalysis, and nanomaterials. She authored and contributed to six scientific papers published on international journals on these topics with two of them in Journal of Catalysis and one in Catalysis Today.