

Synthesis of Gold Nanoparticles Stabilized in Na-Montmorillonite for Nitrophenol Reduction

F. Ammari, M. Chenouf

Abstract—Synthesis of gold nanoparticles 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. In this research field, we used Na-montmorillonite for gold nanoparticles stabilization; various gold loading percentage 1, 2 and 5% were used for gold nanoparticles preparation. The gold nanoparticles were obtained using chemical reduction method using NaBH_4 as reductant agent. The obtained gold nanoparticles stabilized in Na-montmorillonite were used as catalysts for the reduction of 4-nitrophenol to aminophenol with sodium borohydride at room temperature. The UV-Vis results confirmed directly the gold nanoparticles formation. The XRD and N_2 adsorption results showed the formation of gold nanoparticles in the pores of montmorillonite with an average size of 5 nm obtained on samples with 2% gold loading percentage. The gold particles size increased with the increase of gold loading percentage. The reduction reaction of 4-nitrophenol into 4-aminophenol with NaBH_4 catalyzed by Au-Na-montmorillonite catalyst exhibits remarkably a high activity; the reaction was completed within 9 min for 1%Au-Na-montmorillonite and within 3 min for 2%Au-Na-montmorillonite.

Keywords—Chemical reduction, gold, montmorillonite, nanoparticles, 4-nitrophenol.

I. INTRODUCTION

SINCE the pioneering discovery of the high activity of gold nanoparticles in CO oxidation [1], synthesis and application of gold nanoparticles (AuNPs) has attracted significant attention because of their specific catalytic properties in comparison to the bulk material. In catalysis, gold catalysts have been used in selective hydrogenation [2], [3], CO oxidation [4] and water-gas shift reaction [5]. AuNPs were used recently as catalysts in the reduction of 4-nitrophenol to 4-aminophenol [6]-[8].

In addition, 4-aminophenol reaction was used widely as an intermediate for the preparation of analgesic and an antipyretic agent such as paracetamol [9].

It was found, that the size of AuNPs may influence the catalytic activity of gold based catalysts, in general AuNPs aggregation, and then the increase in particles size led to the decrease of their catalytic activity. The key factor for small AuNPs synthesis is the use of stabilizer or a good support. Some metal oxides such as MgO [10], TiO_2 [11] and Al_2O_3 [12] were used to small AuNPs preparation, without the addition of any stabilizer. At the other hand, stabilization of AuNPs can be achieved by using of surfactants [13], ligand

[14] and polymers [15], [16]. Recently, the surfaces of montmorillonite and sepiolite were used to deposition of highly dispersed small [17], [18]. The stabilization of gold nanoparticles in acid-activated montmorillonite porosity was reported [19].

This paper reports AuNPs stabilization in purified montmorillonite without any additional treatment of acidification using a simple method based on chemical reduction method. Here AuNPs were prepared by reducing gold from its salt precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) by sodium borohydride in the presence of montmorillonite as a stabilizer. The catalytic activity of AuNPs stabilized in montmorillonite prepared was then tested in the reduction of 4-nitrophenol using sodium borohydride NaBH_4 as reductant agent. Both purified montmorillonite and gold-montmorillonite were characterized by several methods, UV-Vis spectroscopy, X-ray Diffraction (XRD), transmission electron microscopy (TEM) and N_2 adsorption.

II. EXPERIMENTS

A. Reagents

For samples preparation, natural bentonite, obtained from the Roussel deposit of Maghnia (Algeria), was used as gold-stabilizer after treatment of purification and homoionisation with NaCl , $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich) as gold precursor, NaBH_4 (Sigma Aldrich) as reductant agent and 4-nitrophenol (Fisher Chemical) for catalytic test.

B. Montmorillonite Preparation

Natural bentonite was first purified by sedimentation to remove impurities like sand feldspar and calcite. Typically, 10 g of bentonite was vigorously stirred in 1 l of distilled water for 3 h and kept 24 h 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 $<2\text{nm}$ fraction of montmorillonite were collected and designed as mont.

C. Gold Nanoparticles Preparation

For the preparation of 1,2 and 5wt% Au stabilized in Na-montmorillonite (mont) 10ml of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution (0.01, 0.02 or 0.05g) respectively was reduced with aqueous solution of NaBH_4 in presence of 10ml of mont suspension (0.5g). The NaBH_4 solution was added slowly and the mixture

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was kept under vigorous stirring for 1h at room temperature. After centrifugation and washing of several times with distilled water, the samples were dried overnight at 60°C. The collected samples were designed as 1Au-mont, 2Au-mont or 5Au-mont indicating the percentage of gold used of 1, 2 or 5% respectively. The preparations and storage were performed in the absence of light.

D. Catalytic Reduction of 4-Nitrophenol (4-NP)

The 4-nitrophenol reduction was carried out in the liquid phase at room temperature. Typically an aqueous solution of NaBH_4 was added to 10mg of Au-mont previously dispersed in 10ml of distilled water, at this mixture, an aqueous solution of 4-NP 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 [6]. The reduction process was monitored by UV-Vis absorption spectrometry. Every 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.

E. 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 PANalytical instrument using $\text{CuK}\alpha$ 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.

III. RESULTS

A. Characterization Results

UV-Vis spectrometry results immediately confirmed the AuNPs formation by analysis of gold-montmorillonite suspension during preparation. The results obtained on 1Au-mont, 2Au-mont and 5Au-mont are reported in Figs. 1 (a)-(c), for 1Au-mont sample any absorption band was observed, however, a large band centred at 520nm corresponding to small gold particles was observed on 2Au-mont, this band become more discernible for 5Au-mont. B. J. Borah et al. [19] and C. Lin [20] were observed in the same band. The decrease in the band centered at 520nm is in relation with the formation of smaller gold nanoparticles.

From BET results, a value of surface area of $56\text{m}^2/\text{g}$ was obtained on mont with diameter pore BJH model of 8.5nm. The surface area of mont decrease to $9\text{m}^2/\text{g}$ after insertion of gold particles in 2Au-mont. In addition, the adsorption-desorption isotherms reported in Fig. 2 of mont was of type-IV following IUPAC classification with the presence of H3

hysteresis, indicating mesoporous solid. The decrease in surface area on 2Au-mont can be attributed to AuNPs stabilization within the mesopores of montmorillonite.

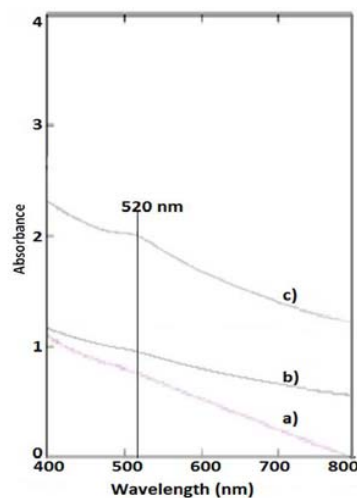


Fig. 1 UV-Vis spectra during preparation, after 30min of stirring obtained on 1Au-mont a), 2Au-mont b) and 5Au-mont c)

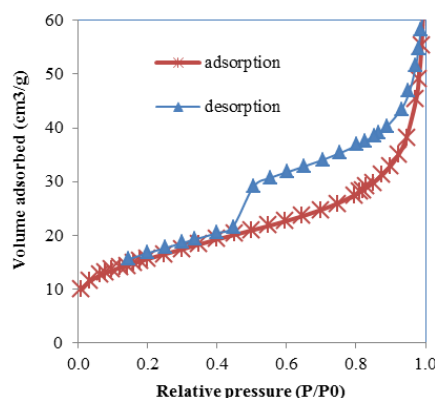


Fig. 2 Adsorption-desorption isotherms of 2%Au-mont

The XRD analysis on Au-mont with different percentage of gold are reported in Fig. 3. The insertion of gold nanoparticles into montmorillonite was also confirmed by the XRD analysis, in addition to typical montmorillonite diffraction peaks (a), four characteristic gold reflections were, Au(111) at 38.2° , Au(200) at 44.5° , Au(220) at 64.6° were observed. XRD spectra reported in $33-40^\circ$ 2θ region was used to calculate gold particles size. A gold particles size estimated by XRD analysis is about 6.5nm for 2Au-mont and 8.7nm for 5Au-mont. For the 1Au-mont, no diffraction line was discerned, because of the too small particle sizes in accordance with UV-vis spectrometry results.

In the TEM images Fig. 4 obtained on 2Au-mont, the gold particles appeared as homogeneously dispersed on montmorillonite. The sizes of most particles are about 4-8nm with average particle size of 5nm, same (smaller fraction) are as large as 8nm.

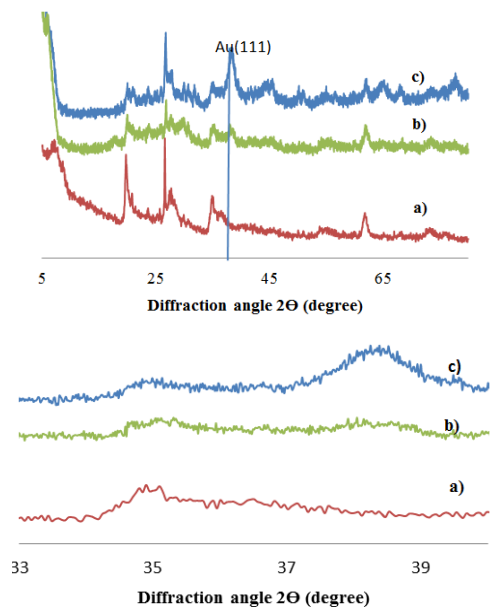


Fig. 3 XRD analysis on mont a) compared to 2Au-mont b) and 5Au-mont c) in 5-80 2Theta region and 33-40 2Theta region

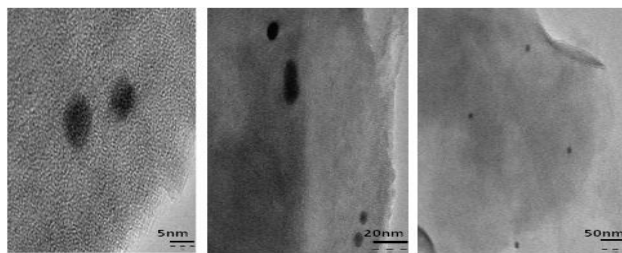


Fig. 4 TEM image of overview of 2Au-mont

B. 4-Nitrophenol Reduction

The catalytic activity of AuNPs 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. 5. 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. The characteristic peak of 4-AP increased rapidly and the reaction was completed within 9min for 1Au-mont and within 3 min for 2Au-mont. The catalytic activity of Au-mont catalysts increased with the increase of loading level of AuNPs.

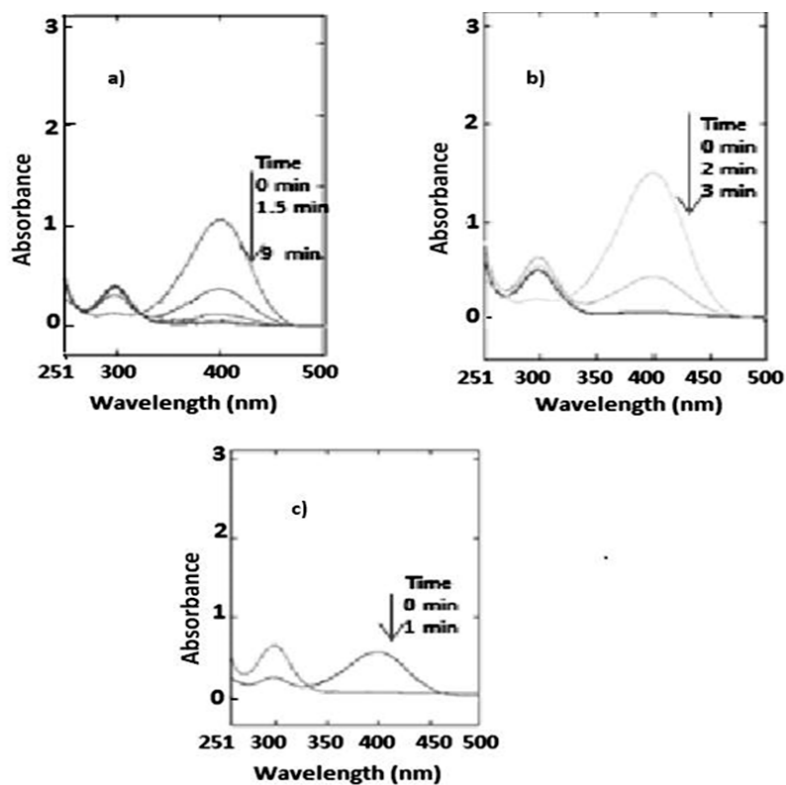


Fig. 5 UV-Vis absorption spectra for 4-NP reduction with an excess of NaBH_4 at room temperature on a) 1Au-mont b) 2Au-mont c) 5Au-mont

The Au-mont was very active for this reaction type, no reduction activity was observed on the stabilizer (mont) alone or without Au-mont catalyst presence. Fig. 6 represents the variation of the $\ln(A_t/A_0)$ versus reaction time calculated from

the absorbance data obtained on 1Au-mont and 2Au-mont, where A_0 and A_t are the initial absorbance of 4-NP and the absorbance of 4-NP at reaction time, t , respectively.

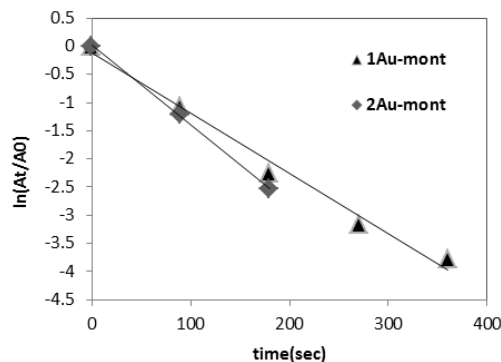


Fig. 6 Plot of $\ln(A_t/A_0)$ versus reaction time of reduction for 1Au-mont and 2Au-mont

A good linear correlation has been obtained, and a calculated value of constant rate is about $1.07 \cdot 10^{-2} \text{ s}^{-1}$ for 1Au-mont and $1.47 \cdot 10^{-2} \text{ s}^{-1}$ for 2Au-mont, this result confirmed the high activity of Au-mont catalyst in the reaction of 4-nitrophenol reduction, this activity increase with increasing gold loading percentage from 1 to 2 to 5%.

IV. CONCLUSION

In summary, gold nanoparticles were successfully prepared using a facile preparation method in the presence of montmorillonite as stabilizer agent. The characterization results confirmed a small gold nanoparticles formation within the mesopores of montmorillonite with an average particle size of 5nm obtained on 2Au-mont. From characterization results, it is evident 1Au-mont exhibit smaller particles size and this gold nanoparticles size increase with increasing the loading level of Au. The catalytic activity of Au-mont was investigated for 4-nitrophenol reduction with an excess amount of NaBH_4 . The reaction followed a pseudo-first-order rate with a constant rate of $1.47 \cdot 10^{-2} \text{ s}^{-1}$ obtained on 2Au-mont; this result confirmed the high activity of Au-mont in 4-NP reduction. This work represents the use of natural montmorillonite for AuNPs synthesis by a simple method, in addition the obtained Au-montmorillonite catalyst is highly active for 4-nitrophenol reduction; this facile preparation method can be used for other metal nanoparticles preparation and other reaction type.

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