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PII: S0925-8388(16)31640-1

DOI: 10.1016/j.jallcom.2016.05.278

Reference: JALCOM 37798

To appear in: Journal of Alloys and Compounds

Received Date: 21 March 2016

Revised Date: 23 May 2016

Accepted Date: 25 May 2016

Please cite this article as: M. Tajbakhsh, H. Alinezhad, M. Nasrollahzadeh, T.A. Kamali, Green synthesis of the Ag/HZSM-5 nanocomposite by using *Euphorbia heterophylla* leaf extract: A recoverable catalyst for reduction of organic dyes, *Journal of Alloys and Compounds* (2016), doi: 10.1016/j.jallcom.2016.05.278.

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Green synthesis of the Ag/HZSM-5 nanocomposite by using Euphorbia

heterophylla leaf extract: A recoverable catalyst for reduction of organic dyes

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ABSTRACT

During this paper, the Ag/HZSM-5 nanocomposite has been successfully synthesized by using an aqueous extract of *Euphorbia heterophylla* leaves as a stabilizing and reducing agent. The green synthesized Ag/HZSM-5 nanocomposite was characterized by FT-IR (Fourier transform infrared spectroscopy), FESEM (field emission scanning electron microscopy), EDS (energy dispersion X-ray spectroscopy), UV-vis, XRD (X-ray powder diffraction) and elemental mapping. The Ag/HZSM-5 nanocomposite was found to be efficient nanocatalyst for the reduction of organic dyes such as Methylene blue (MB), Congo red (CR), Rhodamine B (RhB) and 4-nitrophenol (4-NP) in water at room temperature. The catalytic activities of the nanocatalyst in reactions were monitored by using UV-vis spectroscopy. Interestingly, the Ag/HZSM-5 catalyst can be easily recovered and reused several times without any significant loss of catalytic efficiency.

Keywords: Ag/HZSM-5 nanocomposite; Euphorbia heterophylla; Reduction; NaBH4; Organic dyes

1. Introduction

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Synthetic pigments and dyes have a wide range of applications in cosmetic, textile, drug, printing, foodprocessing industries and their annual production is about $\sim 7 \times 10^5$ tons per year [1-3]. The presence of nitroarene compounds and toxic dyes compounds in aquatic ecosystem is of great concern as these are chemically and biologically stable; therefore, it is difficult to eliminate them by natural degradation processes [4,5]. Hence, there is an urgent need for the development of effective treatment protocols for waste effluents of dye industries.

Although physical and conventional chemical techniques such as adsorption, precipitation and ozonation have been employed for the decolorization of dye effluents, they possess inherent restrictions such as formation of hazardous by-products, high cost and intensive energy requirements [6-8].

Nowadays, due to a higher available catalytic surface, catalysts are more and more used in the form of nanoparticles (NPs). Generally, different synthesis techniques including quick precipitation, sol-gel, electrochemical, sonochemical, microwave irradiation, solid state reaction and alcohothermal synthesis have been applied to the preparation of metal nanoparticles (MNPs) [9-17]. Although, most of these routes are effective but many of them suffer from some disadvantages such as high temperature, harsh reaction conditions, the use of expensive reagents, long reaction times, toxic and hazardous capping agents or stabilizers to control the size and composition of the NPs, the environmental pollution caused by use of organic solvents and low yields of the products.

In addition, separation of the nanosized metal catalysts from the reaction mixture by centrifugation or simple filtration is very difficult. To overcome these limitations, several inorganic materials have been used as support for immobilization of MNPs [18-20]. Among solid supports, zeolites have been reported as efficient catalysts and new class of promising supports for the development of environmentally friendly acidic catalysts [21-23]. As a result of its hydrothermal stability, zeolite has recently been garnering interest as a novel support [24]. In the middle of zeolites, the HZSM-5 zeolite is a medium pore (5.1-5.6 Ű) zeolite with three dimensional channels defined by 10-membered rings [25]. Due to its thermal stability, high acidity, unique shape selective behavior, high surface area and structural network HZSM-5 has been shown to be a stable and effective catalyst for organic reactions [26,27].

Compared to the chemical and physical protocols, environmentally benign production methods of MNPs by applying various bacteria, plants extract and fungus are very attractive [28-36]. The biosynthetic procedures for the synthesis of MNPs have several benefits over physical and chemical synthetic routes, such as simplicity,

cost effectiveness as well as compatibility for biomedical and pharmaceutical applications. So, the use of plants extract in the preparation of MNPs has environmental and economical advantages.

Quite recently, we reported the green synthesis of an Ag/TiO₂ nanocomposite using *Euphorbia heterophylla* leaf extract and its application as a recyclable and heterogeneous catalyst for the reduction of organic dyes [36]. Hence, the Ag/HZSM-5 nanocatalyst was fabricated by applying *Euphorbia heterophylla* leaf extract without any surfactant or stabilizer. The catalytic activity of the Ag/HZSM-5 nanocomposite was investigated for the reduction of 4-NP, CR, RhB and MB using NaBH₄ in water at room temperature and the reactions were checked by UV-vis spectroscopy. More significantly, the catalyst can easily be regenerated and recycled several times without significant loss of catalytic performance. To be an eco-friendly procedure, in spite of its natural availability, biological relevance's and non-toxicity, *Euphorbia heterophylla* has never been explored for the green synthesis of the Ag/HZSM-5 nanocomposite.

2. Experimental

2.1. Instruments and reagents

High-purity chemical reagents were purchased from the Aldrich and Merck chemical companies. HZSM-5 zeolite was prepared according to the literature [23]. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. UV-visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900) to ensure the formation of nanoparticles. Morphology and particle dispersion was investigated by field emission scanning electron microscopy (FESEM) (TESCAN MIRA3). The chemical composition of the prepared nanostructures was measured by EDS analysis. X-ray diffraction (XRD) measurements were carried out using a Philips powder diffractometer type PW 1373 goniometer (Cu K α = 1.5406 Ű). The scanning rate was 2°/min in the 2 θ range from 10 to 80°.

2.2. Preparation of the Euphorbia heterophylla leaf extract

The Euphorbia heterophylla leaf extract was prepared according to our recent work [36].

2.3. Green synthesis of the Ag/HZSM-5 nanocomposite

In a typical preparation of the Ag/HZSM-5 nanocomposite, 50 mL of aqueous solution of AgNO₃ (0.004 M) was gradually added to 25 mL of the plant extract and 1.0 g of the HZSM-5 zeolite with constant stirring at 80 °C for 2 h. After 20 min the color of the solution changed from white to black due to the excitation of surface

plasmon resonance indicating the formation of the Ag/HZSM-5 nanocomposite. Next, the colored solution was centrifuged at 7000 rpm for 30 min to completely precipitation of the Ag/HZSM-5 nanocomposite. The achieved product was then washed several times with ethanol, then air dried for 24 h at room temperature. Next, it was kept under inert argon atmosphere for more precession and protection of our research.

2.4. Catalytic reduction of the 4-NP by Ag/HZSM-5 nanocomposite

In a typical run, 25 mL of the 4-NP aqueous solution (2.5 mM) was mixed with 5.0 mg of Ag/HZSM-5 nanocomposite, stirring constantly for 2 min. Then, 25 mL of freshly prepared NaBH₄ aqueous solution (0.25 M) was added; the reactants were mixed and allowed to stir at room temperature. The yellow color of the solution gradually disappeared, indicating the formation of the 4-aminophenol (4-AP). The reaction progress was checked by UV-vis spectroscopy. Next, the catalyst was simply separated by simple centrifugation and washed successively with water and ethanol, dried and was used for successive runs.

2.5. Catalytic reduction of the MB by Ag/HZSM-5 nanocomposite

In a typical procedure, 5.0 mg of catalyst and 25 mL of the MB aqueous solution $(3.1 \times 10^{-5} \text{ M})$ were mixed in a beaker. Then, 25 mL of freshly prepared NaBH₄ aqueous solution $(5.3 \times 10^{-3} \text{ M})$ was added and the mixture was allowed to stir at room temperature. The progress of the reaction could be checked by the change of the absorption intensity in UV-vis spectrophotometer. After completion of reaction, the catalyst was simply collected from the reaction system by centrifugation and washed successively with water and ethanol and dried for the next run.

2.6. Catalytic reduction of the CR by Ag/HZSM-5 nanocomposite

In a typical experiment, 25 mL of the CR aqueous solution $(1.44 \times 10^{-5} \text{ M})$ was added to 5.0 mg of catalyst. Then, 25 mL of prepared NaBH₄ aqueous solution $(5.3 \times 10^{-3} \text{ M})$ was added and the mixture was allowed to stir at room temperature. The progress of the conversion reaction was then checked by recording the time-dependent UV-vis absorption spectra of the mixture using a spectrophotometer. For the recycling experiment, the catalyst was simply separated from the reaction system by brief centrifugation and washed successively with water and ethanol and dried for the next cycle.

2.7. Reduction of the RhB by Ag/HZSM-5 nanocomposite

Typically, 5.0 mg of catalyst was added to 25 mL of the RhB aqueous solution $(2.09 \times 10^{-5} \text{ M})$. Next, 25 mL of freshly prepared NaBH₄ aqueous solution $(5.3 \times 10^{-3} \text{ M})$ was added and the mixture was permitted to stir at room temperature. The progress of the conversion reaction was then monitored by recording the time-dependent UV-vis absorption spectra of the mixture using a spectrophotometer. At the end of the reaction, the catalyst was simply separated from the reaction system by brief centrifugation and washed successively with water and ethanol and dried for the consecutive cycle.

3. Results and discussion

The stable Ag/HZSM-5 nanocomposite was fabricated via a simple and green method. Facile biosynthesis of the Ag/HZSM-5 nanocomposite using an aqueous *Euphorbia heterophylla* leaf extract has been considered as an easy; cost efficient, eco-friendly, non-toxic and efficient protocol for exploiting *Euphorbia heterophylla* leaf extract. The existence of flavonoid and other phenolics in the extract could be responsible for the reduction of the Ag⁺ ions and formation of the Ag NPs according the following mechanism (Scheme 1).



Scheme 1. Plausible mechanism for the green synthesis of the Ag NPs using Euphorbia heterophylla leaf

extract.

3.1. Characterization of the Ag/HZSM-5 nanocomposite

The structure of synthesized Ag/HZSM-5 nanocomposite was fully characterized by XRD, FE-SEM, EDS, UVvis, elemental mapping and FT-IR.

In a typical synthesis of the Ag/HZSM-5 nanocomposite, for further monitoring, first stable the Ag NPs were separately synthesized by using a simple biological and low-cost approach via reduction of silver nitrate solution with the aqueous *Euphorbia heterophylla* leaf extract as the reducing and stabilizing agent. The characteristics of the obtained Ag NPs were studied using UV-vis and FT-IR techniques in our recent work [36]. The reduction of the Ag⁺ ions into silver particles was monitored by measuring the UV-vis spectrum by diluting a small aliquot of the sample into distilled water. As the *Euphorbia heterophylla* leaf extract was added to silver nitrate solution, the color of the solution changed from faint light to dark brown indicating Ag NPs formation. Therefore, the progress in conversion reaction of the Ag⁺ ions to Ag NPs was followed by a color change and spectroscopic techniques. UV-vis spectrograph of the colloidal solution of silver nanoparticles has been recorded as a function of time. The absorption spectrum (Figure 1) of the dark brown silver nanoparticles solution prepared with the proposed method showed a surface plasmon absorption band with a maximum of 440 nm [36], indicating the presence of the Ag NPs.



Figure 1. UV-vis spectrum of prepared Ag NPs using the aqueous *Euphorbia heterophylla leaves* extract. Reprinted from ref. 36 with permission. Copyright (2016) Sciencedirect.

The FT-IR spectrum of the Ag/HZSM-5 nanocomposite (Figure 6) showed peaks at 1220-1088 and 800 cm⁻¹, which were assigned to SiO₄ tetrahedral units [37]. Two absorbance bands at 3448 and 1633 cm⁻¹ for the O-H stretching vibration due to H₂O interporous structure and H-O-H bending vibration respectively, were also observed. The strong and broad absorbance band at 454 cm⁻¹ was assigned to the T-O bending vibration of the SiO₄ and AlO₄ internal tetrahedral [38].



Figure 2. FT-IR spectrum of the Ag/HZSM-5 nanocomposite.

The X-ray diffraction pattern of the Ag/HZSM-5 nanocomposite is shown in Figure 3. The relative crystallinity of the Ag/HZSM-5 was calculated based on the intensity of the peaks of angle 2θ range (22-25) [39]. The diffraction peaks at $2\theta = 38.5^{\circ}$ and 44.47° were indexed as the (111) and (200) planes of face centered cubic (*fcc*) metallic silver particles [40].



Figure 3. XRD powder pattern of the Ag/HZSM-5 nanocomposite.

The morphology of the Ag/HZSM-5 nanocomposite is revealed by field emission scanning electron microscopy (FESEM). It is clearly observed that the Ag grain pervaded HZSM-5 zeolite surface, which display a good combination between HZSM-5 zeolite and Ag NPs (Figure 4). This is in agreement with that calculated from XRD investigation. Also, FESEM analysis of the nanocatalyst displayed spherical morphology of the Ag NPs on the outer surface of HZSM-5 zeolite.



Figure 4. FESEM images of the Ag/HZSM-5 nanocomposite.

The chemical composition of the Ag/HZSM-5 nanocomposite was determined by Energy Dispersive X-ray Spectroscopy (EDS). In the EDS spectrum (Figure 5), peaks related to Si, Al, O and Ag are observed. The total Ag content was found to be 29.64 wt %. EDX mapping was then performed to study the elemental distribution of the Ag/HZSM-5 catalyst as depicted in (Fig. 6). The elemental mapping images demonstrate that Ag nanoparticles are highly dispersed on the HZSM-5 zeolite surface in agreement with data achieved by XRD.





Figure 6. EDX compositional mapping analysis for Ag/HZSM-5: Elemental maps for (Blue) O, (Green) Al,

(Black) Si and (Red) Ag.

3.3. Catalytic efficiency and application of the synthesized Ag/HZSM-5 nanocomposite for reduction of the 4-NP In the present work, the catalytic activity of the Ag/HZSM-5 nanocomposite was tested by the reduction of 4-NP to 4-AP in the presence of NaBH₄ in water at room temperature as a model reaction (Scheme 2).



Scheme 2. The reduction of 4-NP on the surface of Ag/HZSM-5 nanocomposite.

It is well-known that 4-NP in aqueous solution exhibits a strong absorption peak at 317 nm which is remarkably red-shifted to 400 nm when treated with a freshly prepared aqueous solution of NaBH₄ (Figure 7). The absorption peak at about 400 nm comes from the formation of dark yellow colored 4-nitrophenolate ions (Scheme 3) in alkaline conditions upon the addition of NaBH₄. It was demonstrated that the reduction reaction did not proceed in the absence of the Ag/HZSM-5 nanocomposite and the absorption peak at 400 nm stayed unchanged even for over 100 min. After Ag/HZSM-5 nanocomposite was added into the solution containing 4-NP and NaBH₄, the absorption peak at 400 nm gradually dropped in intensity as the reduction reaction proceeded and a new absorption peak started to appear as a shoulder at 300 nm corresponding to 4-AP which indicated the reduction of 4-NP to 4-AP. The absorption peak at 400 nm is fully removed after 320 s induction period.



Figure 7. Time-dependent UV-visible absorption spectra for the reduction of the 4-NP using Ag/HZSM-5

nanocomposite in aqueous media at room temperature



Scheme 3. The reduction reaction for the conversion of 4-NP to product.

The effects of the amount of the NaBH₄ and catalyst were determined for reduction reaction. As depicted in Table 1, no reaction was achieved in the absence of the catalyst (Table 1, entry 1). So, indicating that the catalytic reduction occurs at the surface of catalyst. The best result was achieved with 100 equivalents of the NaBH₄ and 5.0 mg of catalyst at room temperature (Table 1, entry 5). With an overall look at Table 1, it was observed that the catalytic performance increased with an increase in the amount of the NaBH₄. Moreover, in the presence of 100 equivalents of the NaBH₄ and 5.0 mg of catalyst of the NaBH₄ and 5.0 mg of catalyst, complete conversion was obtained within 320 s. To understand the effect of the Ag NPs on the reduction of the 4-NP, reaction was carried out in the presence of 5.0 mg of the HZSM-5 and 100 equivalents of the NaBH₄ (Table 1, entry 2). In the absence of the

Ag NPs, under the same conditions, the HZSM-5 has a lower rate than the Ag/HZSM-5. The Ag/HZSM-5 shows the fastest rate because of the synergic interaction between Ag NPs and HZSM-5.

Table 1.

Optimization of reaction conditions for reduction of the 4-NP to 4-AP.

Entry	Catalyst (mg)	NaBH ₄ (equivalents)	Time
1	0	50	24 h ^a
2	HZSM-5 (5.0)	100	540 s
3	Ag/HZSM-5 (5.0)	50	640 s
4	Ag/HZSM-5 (5.0)	75	440 s
5	Ag/HZSM-5 (5.0)	100	320 s
6	Ag/HZSM-5 (7.0)	100	320 s

^a No reaction.

The catalytic reduction of the 4-NP to 4-AP is an electron transfer (ET) process. The reaction was carried out in two steps. In the first step of process, 4-NP and BH_4^- diffuse from aqueous solution to the surface of catalyst via π - π stacking interactions. Then the hydrogen atoms, which are formed from BH_4^- , after ET to Ag NPs attack 4-NP molecule. Finally, the corresponding product was desorbed from the surface of the catalyst.

3.4. Catalytic reduction of the RhB, CR and MB

In the present work, we have also studied the catalytic ability of the Ag/HZSM-5 nanocomposite towards the reduction of the MB, CR and RhB with the maximal absorption peak (λ_{max}) at 663, 493 and 554, respectively and results are presented in Table 2. As shown in Table 2, a short time and low amount of catalyst were needed for the reduction of various dyes. The best results were obtained with 5.0 mg of the Ag/HZSM-5 nanocomposite in the presence of freshly prepared NaBH₄ aqueous solution (5.3×10^{-3} M) at room temperature.

Table 2.

Catalytic reduction of the RhB, CR and MB using Ag/HZSM-5 nanocomposite.

Entry	Dye (M)	NaBH ₄ (M)	Catalyst (mg)	Time (s)
1	CR (1.44×10^{-5})	$5.3 imes 10^{-3}$	5.0	100
2	CR (1.44×10^{-5})	$5.3 imes 10^{-3}$	7.0	100
3	RhB (2.09×10^{-5})	$5.3 imes10^{-3}$	5.0	200
4	MB (3.1×10^{-5})	$5.3 imes 10^{-3}$	5.0	94

The catalytic reductions of the MB, CR and RhB were monitored by UV-vis absorption spectroscopy of the reaction mixture after the addition of the NaBH₄ and Ag/HZSM-5 nanocomposite. As can be seen in Figure 8,

the absorption intensity at the absorption peak of MB, CR and RhB decreased as the reduction reaction proceeded. It was observed that degradation of dyes occurred within 94-200 s, depending upon the dye, indicating the Ag/HZSM-5 nanocomposite was able to reduce MB, CR and RhB.





Figure 8. Time dependent UV-vis spectral changes of the reaction mixture of (a) MB, (b) CR, (c) RhB and NaBH₄ catalyzed by Ag/HZSM-5 NPs.

3.5. Catalyst recyclability

Recyclability and stability of the nanocatalyst for the reduction of various dyes via NaBH₄ was tested. The Ag/HZSM-5 nanocomposite can be easily separated from the reaction mixture by mild centrifugation and washed with water and ethanol several times for the successive runs. The regenerated catalyst was recycled five times for 100% reduction of the 4-NP. This recyclability demonstrates the turnover and high stability of catalyst under operating conditions. The leaching of metal from the Ag/HZSM-5 nanocomposite was checked. After the isolation of the catalyst, the reaction solution was analyzed by the AAS (Atomic Absorption Spectroscopy) technique. The result of analysis after fifth runs showed that only a very small amount of Ag metal (less than 1.0%) was leached into the solution.

4. Conclusions

In summary, we have demonstrated an environmentally friendly protocol to prepare stable Ag/HZSM-5 nanocomposite using *Euphorbia heterophylla* leaf extract without using any special capping agents. The flavonoids present in extract of leaves of *Euphorbia heterophylla* act as both capping/stabilizing and reducing agents. The present method is inexpensive, simple, easily scaled up and environmentally benign because it does not require an extra reductant or surfactant template, hazardous materials and organic solvent. The prepared Ag/HZSM-5 nanocomposite capped by biomolecules was characterized by using FESEM, EDS, UV-vis, elemental mapping, XRD and FT-IR techniques. Moreover, the catalytic performance of the Ag/HZSM-5

nanocomposite for reduction of variety of dyes in water was also considered. In addition, the catalyst could be easily isolated from the reaction mixture and successively recovered and reused for five cycles without any significant loss of catalytic efficiency, thus making this procedure environmentally more acceptable. Furthermore, the synthesized catalyst by this protocol is absolutely stable and can be encouraged for a broader range of applications.

Acknowledgments

We gratefully acknowledge the Iranian Nano Council and the Universities of Mazandaran and Qom for the support of this work.

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Highlights:

- Ag/HZSM-5 nanocomposite was prepared using *Euphorbia heterophylla* leaf extract and characterized.
- First report on the use of the Ag/HZSM-5 nanocomposite for reduction of organic pollutant dyes.
- The catalyst is found to be stable and reusable.

Graphical Abstract

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